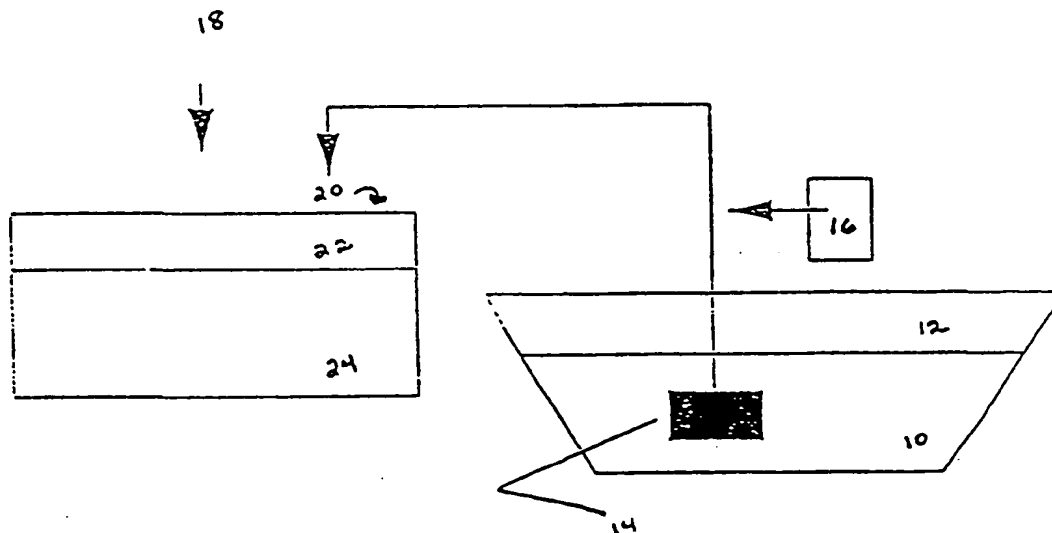




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: B01J 19/08, C07B 63/00	A1	(11) International Publication Number: WO 95/11749 (43) International Publication Date: 4 May 1995 (04.05.95)
(21) International Application Number: PCT/US94/12357 (22) International Filing Date: 27 October 1994 (27.10.94) (30) Priority Data: 08/144,134 27 October 1993 (27.10.93) US (71)(72) Applicants and Inventors: SCRUDATO, Ronald, J. [US/US]; Research Center, 319 Piez Hall, SUNY Oswego, Oswego, NY 13126 (US). ZHANG, Pengchu [CN/US]; 303 Culkin Hall, SUNY Oswego, Oswego, NY 13126 (US). (74) Agent: JOHNSON, John, T.; Heslin & Rothenberg, P.C., 5 Columbia Circle, Albany, NY 12203 (US).		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>

(54) Title: PHOTOCATALYTIC DESTRUCTION OF CONTAMINANTS IN SOLIDS



(57) Abstract

The invention provides an apparatus and method for photocatalytic degradation/destruction of contaminants in solids. The apparatus can be designed for in-situ, on-site, or remote usage, and generally comprises a reactor housing (20) in which solid material is simultaneously exposed to a photoactivatable catalyst (16) and light energy (18). The reactor housing includes a means for agitating the solid material (38) such as a baffle system, to maximize exposure of the solid material to the catalyst and light energy. The method of the invention utilizes photocatalysis to degrade contaminants in/or sorbed to the solid material. The solid material may be separated into a suspended portion within an aqueous source of free radicals and a bottom portion. The exposure of a catalyst to light energy causes the production of free radicals which, when in contact with the contaminants in the suspended portion or the bottom portion, react with the contaminants to degrade the contaminants.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

PHOTOCATALYTIC DESTRUCTION OF CONTAMINANTS IN SOLIDS

Field of the Invention

5 This invention relates in general to the decontamination of solid materials, and more particularly to the photocatalytic degradation of contaminants in solid material such as soils, sediments and sludges.

10 Background of the Invention

Throughout this application various publications are referenced by arabic numerals within parentheses. Full citations for these references may be found at the end of the specification immediately preceding the claims. The disclosures of these publications in their entireties are hereby incorporated by reference in this application in order to more fully describe the state of the art to which the invention pertains.

20 The industrialization of many countries, including the United States, has led to the introduction of many pollutants or contaminants into natural ecosystems. Such ecosystems invariably include water systems, where the majority of contaminants become associated with solid materials,

-2-

such as the soils and sediments, in the water systems. For example, contaminants may settle to the bottom of a river or lake. There has been a growing concern from the standpoint of preserving the environment in cleaning up these contaminants.

A potential method for such clean-up is through the use of environmental photochemistry. Environmental photochemistry seeks to utilize photocatalysis in the destruction or degradation of the contaminants from the environment. Photocatalysis refers to the use of light energy to catalyze chemical reactions.

One example of such contaminants, polychlorinated biphenyls (PCBs), have been widely used as dielectric fluids in transformers and as hydraulic and heat transfer fluids since the 1930s. Following enactment of the Toxic Substances Control Act (TSCA) and the Resource Conservation and Recovery Act (RCRA), PCBs were cited as posing severe environmental threats and their use was restricted. Significant quantities of PCBs are still contained in functioning electrical equipment, and the periodic uncontrolled loss of PCBs from transformers and capacitors results in soil and surface contamination above the regulatory limit. Clean-up procedures must be used, often necessitating excavation of the contaminated area.

Extensive studies have been conducted during the last two decades on many aspects of PCBs including their physiochemical properties, toxicity to wildlife and humans, distributions, and remediation of contaminated water and land. These studies lead to the conclusion that removal of PCBs is desirable in many instances.

-3-

Extraction has been utilized to remove PCBs in soils, sludges and/or sediments by extracting with organic solvents, gas streams, oil, and supercritical fluid of carbon dioxide. The extraction processes are operated at various temperatures and pressures, and are commonly followed by solvent/water/pollutant separation and PCB concentration processes.

Solidification/stabilization have also been utilized to immobilize PCBs in media with cementitious grout compounds and chemical stabilizers to produce a cement-like mass. The created monolith should be impermeable and able to withstand environmental stresses such as freeze/thaw cycles, immersion in groundwater, and cap construction.

Physical and biological processes are used to destroy PCBs. Incineration has been commonly used to destroy PCBs, but the high cost and production of hazardous by-products limits its application. Anaerobic and aerobic biodegradation has been used for PCBs-contaminated media treatment, but is slow and perhaps only partially capable of producing less hazardous compounds.

It is known from laboratory experiments that chemical processes such as hydrogenation, polymerization, base-catalysis, and oxidation are able to dechlorinate PCB congeners or alter the congeners' structure. These processes can create less toxic and/or more readily decomposable substances through other processes. Photocatalytic processes have been introduced to decompose PCBs in waters. These processes use solar energy to break down the PCBs.

Photocatalytic degradation of PCBs in solid materials may offer another alternative for PCB

-4-

clean-up, and has long been desirable but little progress in this area has been made.

Photodegradation of PCBs present in or bound on solid materials offers an attractive remediation potential because it is relatively rapid, degradation can be accomplished within minutes or hours (1-4), the reaction can be conducted with sunlight (3-6) and/or artificial light, catalysts are abundant and low cost (1,3,4,7), and PCB congeners and other contaminants may be completely mineralized (1,4).

Earlier studies on photo-degradation, -destruction, -dechlorination, and -decomposition were carried out with artificial UV light sources, lightly chlorinated PCB congeners (mono- and di-chlorinated biphenyls), or in pure aqueous solutions and/or organic solvents (1-9). These previous studies contributed to an understanding of the photocatalytic processes of PCB degradation in aqueous solutions and demonstrated the potential to remediate PCB-contaminated waters. There are no reported studies on the efficiency of catalyst induced photodegradation on environmental samples such as soils and sediments contaminated by organic substances and irradiated by sunlight and/or artificial light.

Another common contaminant of ecosystems are microorganisms, such as Escherichia coli which can indicate fecal contamination of some aquatic systems. Ireland and co-workers were the first to report inactivation of this microorganism in waters using titanium dioxide as a photocatalyst (10).

The photolysis in different aquatic media and under laboratory conditions has also been studied for various pesticides and herbicides. These studies

-5-

have shown differences in the degradation rates as well as product distribution between natural and distilled waters, resulting from the presence of particulate and dissolved substances in natural waters which influence photolysis through attenuation of sunlight, secondary photoreactions, and chemical or physical interactions that change the speciation and availability of pesticides and herbicides (18-21). Suspended and dissolved materials in natural water not only affect the photodegradation rate of pesticides and herbicides, but the photoproducts may also be different from that generated in pure water solutions (22).

Thus, numerous compounds have been decomposed in aqueous systems by irradiating in the presence of titanium dioxide (1,3,4,11-17). However, suspended particles in natural water can significantly alter the pathways and efficiencies of photolysis of organics, such as PCBs, in different ways.

Thus, a need continues to exist for a method of cleaning up contaminated solids such as soils, sediments, and sludges. The success of a technology for soil and/or sediment remediation depends on the amount of media it can handle, the time needed to reach the designated treatment goal, and the costs required to operate the system. The key to achieve these is to establish a process that can rapidly destroy contaminants in a simple operational configuration using minimum energy.

30 Summary of the Invention

The primary objective of the invention is to provide such a practical, low cost and efficient process to degrade contaminants, such as PCBs, in

-6-

sediments and other solids, to the extent that the residual concentrations of the contaminants do not pose a threat to human health or the environment.

In accordance with this objective, the subject invention provides a method and apparatus for the photocatalytic degradation of contaminants in solid material. The apparatus includes means for containing a solid material; means for agitating the solid material within an aqueous source of free radicals, thereby separating the solid material into a first portion suspended in the aqueous source and a second portion deposited below the aqueous source; and means for simultaneously exposing the first portion to a photoactivatable catalyst and light energy.

The method according to the subject invention comprises selecting a solid material containing contaminants therein; placing the solid material in a reactor housing containing an aqueous source of free radicals; agitating the solid material, so as to separate the solid material into a first portion suspended in the aqueous source and a second portion deposited below the aqueous source; introducing a photoactivatable catalyst into the reactor housing; and exposing the photoactivatable catalyst to light energy, thereby causing reaction of the catalyst with the aqueous source of free radicals to generate the free radicals, which contact the first portion of the solid material suspended in the aqueous source and degrade the contaminants therein.

An apparatus is also provided for photocatalytic degradation of contaminants in solid materials, which comprises means for containing a solid material, means for agitating the solid material within an

-7-

aqueous source of free radicals, and means for simultaneously exposing the solid material to a photoactivatable catalyst and light energy. In this embodiment, the solid material is selected and
5 treated in-situ or is placed in a reactor housing, then dampened with an aqueous source of free radicals and agitated in the presence of the catalyst and light energy. Agitation can be by continuously plowing the solid material to turn the solid material
10 over and over.

The process of the subject invention is preferably operated at ambient pressure and temperature. The catalyst to be used is preferably titanium dioxide which is environmentally inert,
15 although other catalysts can also be used. The photocatalytic process can take place under irradiation of artificial and/or solar light. The technology is thus safe, requires low energy and provides for in-situ and/or on-site remediation of
20 highly contaminated sediments, soils, and/or sludges.

Brief Description of the Figures

These and other objects, features and advantages of this invention will be evident from the following detailed description of preferred embodiments when
25 read in conjunction with the accompanying drawings in which:

Fig. 1 is a schematic for an on-site reactor which is one embodiment of the subject invention;

Fig. 2 is a schematic for an in-situ reactor
30 which is another embodiment of the subject invention;

Fig. 3 illustrates a series of three reactors connected in series and equipped for recirculation;

-8-

Fig. 4 illustrates a baffle design for one of the reactors shown in Fig. 3;

Fig. 5 is a plan view of a further reactor design according to the subject invention;

5 Fig. 6 is a cross-sectional view of the reactor design shown in Fig. 5;

Fig. 7 is a cross-sectional view of another embodiment of a reactor design according to the subject invention;

10 Fig. 8 is a schematic of the connection of a series of photoreactors according to an additional embodiment of the subject invention;

Fig. 9 is a schematic showing the process of treatment of contaminated sediment according to one
15 embodiment of the subject invention;

Fig. 10 shows the photodecomposition of AroclorTM 1248 in clay suspension in the presence of titanium dioxide;

20 Fig. 11 shows the relative concentration changes of PCB congeners in clay suspension after irradiation;

Fig. 12 shows the photodecomposition of PCBs in the Grasse River sediment suspension;

25 Fig. 13 shows the relative concentration changes of PCB congeners in the Grasse River sediment suspension after irradiation;

Fig. 14 is a GC/MS chromatograph for PCB congeners with 1-3 chlorines in the Grasse River sediment extraction blank;

30 Fig. 15 is a GC/MS chromatograph for PCB congeners with 1-3 chlorines in the Grasse River sediment extraction after 2 hours exposure to titanium dioxide;

-9-

Fig. 16 is a GC/MS chromatograph for PCB congeners with 1-3 chlorines in the Grasse River sediment extraction after 6 hours exposure to titanium dioxide;

5 Fig. 17 is a GC/MS chromatograph for PCB congeners with 4-6 chlorines in the Grasse River sediment extraction blank;

10 Fig. 18 is a GC/MS chromatograph for PCB congeners with 4-6 chlorines in the Grasse River sediment extraction after 2 hours exposure to titanium dioxide; and

15 Fig. 19 is a GC/MS chromatograph for PCB congeners with 4-6 chlorines in the Grasse River sediment extraction after 6 hours exposure to titanium dioxide.

Detailed Description of the Invention

The apparatus of the subject invention provides for the photocatalytic degradation of contaminants in solid material, such as sediment, soil, or sludge.

20 The main components of the subject invention are a means for containing a solid material, a means for agitating the solid material within an aqueous source of free radicals, and means for simultaneously exposing the agitated solid material to a

25 photoactivatable catalyst and light energy.

More particularly, a solid material is placed in a reactor housing. The housing can comprise any suitable shape or form. For example, a caisson which is a large diameter pipe can serve as the housing in

30 an in-situ application. An additional "housing" might include a natural or constructed pond or lake which can be used to contain the material to be treated or can be the photocatalytic reactor vessel.

-10-

A large vat can serve as the housing in an on-site or remote application. Once the solid material is contained within the housing or enclosure, the solid material is subjected to continuous agitation within an aqueous source of free radicals. The relevance of the source of free radicals is described in further detail below.

The agitation is preferably accomplished utilizing moving baffles within the reactor housing or by utilizing a dredge located within a caisson in an in-situ application. The baffles may be mounted to a rotating boom. The agitation separates the solid material into a first portion suspended in the aqueous solution and a second portion deposited below the aqueous source. For further agitation of the suspended portion, the baffles can be movably positioned within the suspended portion. For further agitation of the bottom portion, the baffles can be, for example, plow-shaped, and be positioned at the lower level of the bottom portion. Agitation of the solids to be treated may also be accomplished by air and/or water induction.

The first suspended portion is then exposed simultaneously to a photoactivatable catalyst and light energy. Contaminants within the first portion are thereby degraded by the action of the catalyst, activated by the light energy. Suitable catalysts for such an application include catalysts comprising semiconductor materials, such as titanium dioxide or zinc oxide. Other suitable photoactivatable catalysts will be readily apparent to those skilled in the art.

The continuous agitation causes the suspended portion to be in constant motion, thereby maximizing

-11-

exposure to the catalyst and light. For example, maximum exposure occurs at the surfaces of the aqueous source. This may be at the top surface if the light energy is being applied from above the aqueous source at the top of the reactor housing, or at the side surfaces of the contained solution if light is being applied from the sides of the reactor housing (i.e. with a glass-walled reactor housing). The agitation causes the aqueous solution containing the suspended portion to "roll" past the light surfaces continually.

The bottom portion of the solid is also treated to maximize exposure to the catalyst and light energy, so that contaminants therein are degraded. This can be accomplished in several ways. For example, the suspended portion can be removed from the reactor by suitable means (i.e. gravity or pumped) when its treatment is complete. This will reveal the bottom portion. A small amount of the aqueous source of free radicals is left overlying the bottom portion, to serve as the source of free radicals. After the removal of the suspended portion and the majority of the aqueous source, the bottom portion is in contact with the catalyst and light energy simultaneously. Therefore, degradation at the surfaces of the bottom portion can occur. (Note that degradation of the bottom portion at the sides if glass-walled reactors are utilized would have been occurring prior to the removal of the suspended portion.) After removal of the suspended portion, the top surface of the bottom portion is also subjected to degradation. Baffles or other suitable systems can be used within the bottom portion at this point to further agitate the bottom portion, again

-12-

maximizing exposure by causing the bottom portion to continually "roll" past the surfaces where simultaneous exposure to catalyst and light occur.

5 In another embodiment, the bottom portion can be removed from the reactor housing and transferred to a secondary or tertiary reactor housing. Removal can be by any suitable means, such as an auger or wormscrew, conveyor, gravity flow or pumping. Once placed in a secondary or tertiary reactor, the bottom
10 portion can again be mixed with an aqueous source of free radicals to create a new suspended portion and a new bottom portion. Alternatively, the bottom portion can be continually agitated within the second housing.

15 The treated suspended portion can also be transferred to a series of reactor housings for further treatment and exposure to catalyst and light.

Numerous contaminants known to those skilled in the art can be removed by such photocatalysis. These
20 include, but are not limited to, organic contaminants such as polychlorinated biphenyls (PCBs), microorganisms such as Escherichia coli, select inorganic contaminants such as metals, and pesticides, fungicides, and insecticides.

25 To elaborate further on the type of contaminants that can be removed according to the subject invention, the examples include non-aromatic chlorinated hydrocarbons (chloromethane; tetrachloroethylene; dichloromethane; dichloroethane;
30 trichloromethane; 1,1 dibromoethane; carbon tetrachloride; 1,2 dibromoethane; dibromomethane; ethylene dibromide; tribromomethane; monochloroacetic acid; trichloroethylene; and dichloroacetic acid); aromatic chlorinated hydrocarbons (PCBs; 1,2,4

-13-

trichlorobenzene; dioxins; 3,3 dichlorobiphenyl;
chlorobenzene; 2,4,5 trichlorophenoxyacetic acid; and
4,4' DDT); aromatic and non-aromatic hydrocarbons
(benzene; alkanes; toluene; alkenes; xylene; alkynes;
5 and ethyl benzene); surfactants (sodium
dodecylbenzene sulphonate); organic acids (salicylic
acid; butyric acid; acetic acid; propionic acid;
formic acid; octanoic acid; oxalic acid; and pyruvic
acid); phenols (phenol; 4-chlorophenol; 1-
10 chlorophenol; 3,4 dichlorophenol; 2-chlorophenol;
pentachlorophenol; and 2,4,5 trichlorophenol);
nitrogen containing organics (2,4 dinitrotoluene;
benzonitrile; nitrobenzene; nitriles; aniline;
caprolactam; proteins; and cyanide); inorganics
15 (lead ions; chromium ions; mercury ions; and copper
ions); insecticides (chlorpyrifos - phosphorylated
pyridine; endosulfan - chlorinated cyclodiene; and
permethrin - pyrethriod); herbicides (pronamide -
amide); and fungicides (dichloran - chlorinated
20 nitroaniline; triadimefor - triazole). Also included
as contaminants are microorganisms, such as
Escherichia coli and various other bacteria, viruses,
and pathogens.

The source of free radicals can derive from any
25 suitable source, such as water. The catalyst will
cause the release of free radicals from the water
molecules upon exposure of the catalyst to light
energy in the presence of the water. Similarly,
enhancers can be utilized to increase the
30 availability of free radicals. For example, hydrogen
peroxide can also provide such free radicals or be
used to enhance the production of free radicals,
since exposure of the hydrogen peroxide to the
catalyst in the presence of light energy also

-14-

releases free radicals. The released free radicals will react to degrade the contaminants within the solid material. Other suitable enhancers known to those skilled in the art can also be utilized.

5 Various sources of light energy can be utilized, including natural or artificial. Natural sunlight, UV light, sunlamps, etc., used individually or in concert, can provide the required light energy to activate the catalyst for production of the free
10 radicals.

It is also often desirable to include a means for removing the by-products of degradation, such as volatiles from PCBs degradation. This can comprise any suitable means, such as a granular activated
15 carbon filter.

It should be readily apparent from the description of the invention that various structures can be utilized to accomplish the objectives of the subject invention. Several such structures are
20 described herein by way of example only.

Referring to Figure 1, there is shown an on-site schematic for the photocatalytic degradation of PCB-contaminated sediments and water. A suction dredge 14 or other delivery system transports contaminated
25 sediments 10 which underly water 12 to a photoreactor 20. The contaminated sediments may, for example, be at the bottom of a pond, lake or river. Titanium dioxide catalyst 16 is added to the contaminated sediments as they are transported to the photoreactor
30 20. A solar or artificial light source 18 is placed over the photoreactor 20, and within the photoreactor 20, water 22 overlies the removed contaminated sediments 24. The process according to the subject invention, involving agitation and simultaneous

-15-

exposure to catalyst and light energy, then takes place in the photoreactor.

Referring to Fig. 2, there is shown a cross-sectional schematic of an in-situ process for photocatalytic degradation of PCB-contaminated sediments. A body of water 26 is selected in which a layer of contaminated sediments 28 overlies clean sediments 30, with a layer of shallow water 32 overlying both. A portion of the body of water 26 is encased by a large diameter caisson 44 which is driven or vibrated through the sediments. Solar light or artificial light 40 is emitted through a transparent layer 34 or from within the caisson and titanium dioxide is introduced to the slurry created by the suction dredge 38 via metering pumps 36. Produced volatiles are trapped and treated at 42, a granular activated carbon trap. The system is operated until sufficient treatment is affected and then the caisson is removed and relocated to treat another area.

For the in-situ treatment, as illustrated in Fig. 2, a large diameter steel cylinder or caisson 44 is driven or vibrated using standard construction techniques through the layer of contaminated sediments 28 into the uncontaminated sediments 30. The sediments are situated below shallow waters 32. A pumping system or dredge 38 is used to agitate the sediments to create a sediment/water slurry and to maintain the suspension. The catalyst is introduced as a fine powder with the use of metering pumps 36. The steel cylinder is covered with a transparent layer of plastic or glass 34 to allow sunlight penetration. Artificial sunlight or UV lamp energy sources can also be used to enhance the process. All

-16-

produced gases and volatilized contaminants are collected and passed through a granular activated carbon filter 42 and then returned to the cylinder to assist with maintaining the suspension. The
5 agitation of the sediments is controlled to maintain the optimal concentration of suspended sediments to maximize light and catalyst contact. Although a negative atmosphere will be maintained during the treatment process, the cylinder will be accessible
10 through a hermetically sealed hatch to enable maintenance and sampling.

If the reactor is to be operated as an on-site treatment system, the suction pump (dredge) will be used to carry the suspended sediments to a
15 photoreactor which is located in proximity to the caisson or enclosure system (see Fig. 1). After treatment the sediments can be returned to the cylinder, allowed to settle and once settling has occurred, the cylinder can be removed and used to
20 treat other areas requiring decontamination.

Fig. 3 shows another embodiment of the invention, in which the reactor consists of a series of parallel photoreactors 46, 48, 50 that are connected in series to provide multiple levels of
25 exposure and treatment. The first photoreactor 46 will receive contaminated sediments from a dredge, backhoe, or other delivering device. The sediment slurry will be discharged directly into photoreactor 46 which will be continuously agitated to allow
30 thorough separation of the suspended and bottom sediment fractions. Titanium dioxide catalyst will be introduced at the time the slurry is discharged to photoreactor 46. This photoreactor is designed to maximize exposure to artificial UV and/or sunlight

-17-

sources and as the agitation proceeds, the suspended fraction will be irradiated at the slurry/air surface to promote photocatalysis.

Once the separation has occurred, the suspended sediment fraction will be slowly discharged 52 to photoreactor 48. This phase of the separation will be timed to optimize the discharge rates with the degree of photodegradation. Slow discharge from 46 to 48 will continue until the suspended sediment fraction is thoroughly transferred to photoreactor 48 which will expose the bottom sediments in photoreactor 46 to the light source(s). Agitation of the bottom sediments in photoreactor 46 by a tank baffle or other system will be continued to spread the bottom sediments to maximize contact with the catalyst and radiation to promote photocatalytic degradation.

Following continued treatment in photoreactor 48, the suspended sediment fraction will be gravity discharged 54 or pumped to another photoreactor 50 for continual treatment and for eventual removal and/or discharge 58. Once the bottom sediments in photoreactor 46 have been adequately treated, they will be removed for alternative treatment or disposal 56.

A holding tank 64 can be used for sediment settling and make up water can be pumped back to 46 if needed. The entire system of reactors, 46, 48, and 50, are covered by transparent material and artificial light can also be added.

As shown, initial separation of sediment into component fractions, specifically the suspended and bottom sediments, will occur in photoreactor 46. The sediment will be agitated and kept suspended as well

-18-

as disturbed by a paddle system 66 as shown in Figure 4 and discussed more fully below.

To prevent loss of PCBs and/or other contaminants through volatilization, gases produced during the treatment process will be drawn through an adsorbing/absorbing filter and the exhaust gases may be utilized to disperse the water/sediment mixture to maintain suspensions. The treatment system is designed to allow continuous recirculation 62 thereby enabling extended times of exposure to the catalyst and to sunlight.

Design considerations can also include condensation and water vapor separation.

The fine-grained sediment portion will be moved through each treatment chamber by a mechanically operated paddle section. As shown in Figure 4, the paddle 66 or "agitation board" can be operated in two modes. In photoreactor 46, the suspended sediment is kept in suspension by the back and forth motion of the board. If it is decided to move the bottom sediment to one end of the photoreactor for collection and removal, the board is operated in a lower position to come in contact with the bottom of the vessel and drag the bottom sediments to either end of the photoreactor. While in the lowered position, the door can also be used to agitate the bottom sediments as well as to maximize exposure to the catalyst and light energy.

Figs. 5 and 6 depict the design for another embodiment of an onsite photoreactor. The reactor unit 72 is designed to batch treat bottom and suspended sediments, and has an outer spill containment tank 70. The bottom sediments are emersed under water. The sediments will be

-19-

continually mixed using a series of baffles 74 which will be designed and operated to thoroughly stir the sediments to continually mix and expose the sediments to the light which will be sunlight and a series of artificial lamp sources. A wormscrew 78 or other mechanism will be used to mix and carry sediment out of the reactor. In the cross-sectional perspective of the reactor (Fig. 6), the sump 76 and wormscrew 78 illustrate a method to remove the treated sediment from the reactor to minimize the removal of water. The sediments will be moved along the bottom of the reactor with the use of the baffles 74. The sump and wormscrew can also be used to remove the partially dewatered sediment and to collect samples for analysis during operations. A double sump/wormscrew system for each reactor will provide redundancy as well as accelerate removal of the treated sediment.

Fig. 7 shows an alternative design in which the baffles 80 are rotated on boom 82, agitating the sediment beneath the light source 84. The sediment is removed via wormscrew 86.

Fig. 8 shows a series of photoreactors 92, 94, 96 which are interconnected in spill containment housing 90. The contaminated sediment is delivered to photoreactor 92. Photoreactor 92 separates the coarser grained material from the finer, suspended sediment. The coarser material is transported to reactor 98, within spill containment housing 100, for treatment and eventual discharge to a disposal site 102. The suspended (fine-grained) material is discharged to reactor 94 and then to reactor 96 for continued treatment and eventual discharge to the disposal site 104.

-20-

As shown in Fig. 9, pretreated sediments can be ground and disaggregated in a grinder 122 to reduce the size of clay clumps, grind twigs, leaves and other vegetative matter. The ground material can then be placed in a dispersal chamber or mixing tank 124 that will further segregate the sediments based on size (specific gravity). The sediment will be segregated into two size fractions and after separation, transferred to two separate reactors, treatment ponds or tanks 128 and 130 where titanium dioxide 126 will be introduced through a metering system. The coarse fraction will be placed in reactor 130, and the fine fraction will be placed in reactor 128. The two separated fractions will be subjected to varying times of exposure to sunlight and/or artificial sunlight in the presence of finely ground titanium dioxide in the reactors. In order to maximize exposure to sunlight and contact with the catalyst, the suspension will be continually agitated as it is carried through the reactors. To prevent loss of PCBs through volatilization, gases produced during the treatment process will be drawn through a granular activated carbon filter 132 and the exhaust gases 140 will be utilized to disperse the water/sediment mixture. The treatment system has been designed to allow continuous recirculation through reactor settling tanks 134 and 136, thereby enabling extended times of exposure to the catalyst and to sunlight. Treated and decontaminated effluent 138 can be discharged from the reactor settling tanks 134 and 136.

It is also possible to separate out the catalyst after use, saving expense by recycling the catalyst. This can be accomplished by coating sand grains with

-21-

the catalyst or possibly using ilmenite which is an iron titanium oxide mineral or perhaps titanium oxide-coated magnetite in order to magnetically separate the catalyst from the treated sediment to recover as much of the catalyst as is practical. Other physical or mechanical separation techniques to remove the catalysts can also be utilized.

The feasibility of the above described embodiments of the subject invention are supported by the experimental data obtained in remediation of PCBs-contaminated sediment and bacterially contaminated suspensions. These experimental details are provided below.

Example I

This example details the photodecomposition of PCBs using titanium dioxide as a catalyst and promoted by sunlight in a clay suspension and contaminated sediment. The titanium dioxide catalyzed photolytic process destroyed almost 80% of the total PCBs in the clay suspension after 4 hours of radiation, and greater than 50-60% of total PCBs were destroyed in the sediment suspension within 6 hours.

Two separate experiments were conducted including PCB-contaminated clay in water and a contaminated sediment/water system.

The AroclorTM 1248 standard was obtained from Analabs (North Haven, Conn.), and the stock solution was made by dissolving 32.2 mg of the Aroclor into 100.0 ml of optima grade hexane (Fisher Sci., Rochester, NY). In the clay phase of the experiment, a well crystallized kaolinite from the Source Clays

-22-

Repository (Clay Minerals Society, Columbia, MO) was utilized. Sediment was collected from the Grasse River and provided by the Wadsworth Center for Laboratories and Research, New York State Department of Health (Albany, NY) from the Grasse River, near Massena, NY. The total PCB concentration of the sediment sample was 118 mg/kg. Titanium dioxide (P25) was obtained from Degussa (Teterboro, NJ). The x-ray analysis indicated that anatase is the predominate mineral. The titanium dioxide had an average mean diameter of about 30 nm and an average surface area of 50 m²/g. All water used in this study was prepared by a Nano Pure Water System (Millipore Corp.).

15 Samples were prepared and irradiated as follows:

PCB-Clay Suspension: Five grams of kaolinite were mixed with 25.0 ml of Aroclor 1248 hexane stock solution. The slurry was dried at room temperature for 24 hours before suspending into 500 ml of deionized water. A teflon-coated magnetic bar was used to stir the suspension for two days and then 10.0 ml of the suspension was pipetted into an Erlenmeyer flask with 490 ml of water to make up a PCB-clay working solution. The final PCB-clay suspension contained 0.2 g/L clay and 0.32 mg/L PCBs.

25 Sediment Suspension: Five grams of Grasse River sediment (wet) were suspended into 2 liters of water. After two hours of continually stirring, the large pieces and sands were allowed to settle and after five minutes, the suspension was decanted and the large fraction discarded. The suspended fraction was collected and brought to the final volume of 2.0 L. The suspension was then divided into 5 equal portions of 400 ml.

-23-

Irradiation: One ml of titanium dioxide suspension at a concentration of 50 g/L was pipetted into those samples in which the catalyst was used. Samples that did not contain titanium dioxide served as experimental blanks. Samples containing titanium dioxide wrapped with aluminum foil to avoid irradiation were used as experimental controls. For the PCB-Clay experiment, a PCB-Clay suspension sample was wrapped with foil to compare against the suspension exposed to sunlight (Control I in Fig. 10). All of the sample containers were carefully sealed after insertion of a teflon coated magnetic stirring bar. The irradiation was carried out on the roof of a building at the State University of New York at Oswego (43°N, 76.5°W). Samples were exposed to sunlight during the hours of 12:00-18:00 on bright sunny days with the temperature around 23 +/- 3°C. The flasks used for irradiation were Pyrex glass which allowed visible and near UV wavelength to penetrate into the suspensions. After a specific irradiation time, select flasks were wrapped with aluminum foil but left on the roof and stirred until the last irradiation period was completed. All samples were then taken to the laboratory and stored in the dark overnight in order to allow any PCBs in the head space to equilibrate with the solution.

PCB Extraction and Analysis

Approximately 50 ml of hexane was used to rinse each experimental Erlenmeyer flask three times after the aqueous solution or suspension was removed into a 1 L separatory funnel. The hexane solution was also added to the funnel. The solution was vigorously shaken for one and a half minutes, and then allowed to phase separate. The hexane solution was collected

-24-

in a 250 ml beaker containing about 10 g of Na_2SO_4 to absorb the water brought in with the hexane solution. The extraction process was repeated three times for all samples. The hexane solution was then
5 transferred to a Kuderna-Danish condenser and concentrated on a steam bath. The concentrated hexane solution was passed through a 4% deactivated Florisil column to remove polar compounds. After Florisil clean-up, the hexane solution was again
10 concentrated and then adjusted to the final volume for chromatographic analysis. Experimental controls and blanks were used under the same conditions for each experimental treatment and they were extracted with the same procedure.

15 PCB concentrations were determined on a gas chromatograph (Perkin-Elmer, Sigma 2000) with an electron capture detector (ECD). The temperature program was 100°C for 2 minutes, then increased to 160° at a rate of $10^\circ/\text{minute}$ and further increased at
20 $3^\circ/\text{minute}$ to the final 270° . The GC was equipped with a 0.20 mm x 25 m "Ultra 2" HP glass capillary column. The PCB standard solution was prepared and provided by the New York State Department of Health. A personal computer equipped with a HP/ChemStation
25 software package through an interface (HP 35900) was used to collect and analyze the chromatographic data. Integrated chromatographic peak area sums were utilized to indicate relative changes in PCB concentration. Relative changes in single congener
30 concentrations were done in the same manner.

A GC (HP 5890II)/MSD (HP 5971) was used for congener identification. The entire process was controlled by a HP 486 PC with a software package (HP G1034B) for GC/MSD. To increase the sensitivity of

-25-

the mass spectra, SIM (Selective Ion Monitoring) was chosen to determine the PCB congeners with one to nine chlorines.

Results were as follows:

5 PCB-Clay Suspension: The results of photocatalytic decomposition of PCBs in the clay suspension are illustrated in Fig. 10 and Table 1. The blank represents no titanium dioxide; Control I represents no titanium dioxide and in the dark; and
10 Control II represented titanium dioxide but in the dark. It was observed that there were only slight differences in total PCB concentrations among the Aroclor-clay suspension, wrapped Aroclor-clay suspension, and the wrapped Aroclor-clay-titanium
15 dioxide suspension. Total PCB concentrations dramatically decreased in the clay suspension in the presence of titanium dioxide. After 2 hours irradiation, only 23% of the PCB remained in the
20 suspension and only 19% of the total PCBs was recovered in the sample exposed to sunlight for 4 hours. The relative concentration changes of individual PCB congeners are illustrated in Fig. 11. C is the congener concentration after irradiation, and C_0 is the initial concentration. These data also
25 demonstrate that congeners with low chlorine content were subject to more rapid decomposition from both the 2 and 4 hour irradiation samples than the highly chlorinated congeners. The distribution of C/C_0 in the 2 hour sample had a greater degree of scatter
30 than that of the 4 hour exposure. This suggests that in the initial stages, many low chlorine content congeners were the main targets of the photocatalytic process. When the concentration of the lower chlorinated congeners was reduced, the higher

-26-

chlorinated congeners were subjected to more intensive photodestruction, therefore, expressed in a higher decomposition rate.

Sediment Suspension: After 2 hours irradiation, the total PCB concentration decreased to about 78% of the PCBs recovered from the experimental blank; greater than about 50-60% of the total PCB concentration was lost in the sample exposed to sunlight for the 6 hour exposure (Fig. 12 and Table 1). In Fig. 12, the blank represents no titanium dioxide and the Control represents titanium dioxide but in the dark. The trend evident from Fig. 13, in which C is the congener concentration after irradiation and C_0 is the initial concentration, is that the low chlorine content PCB congeners have a much higher reactivity than the congeners with more than 5 chlorines. The congeners which appear before 23 minutes retention time in the chromatograph usually have 3 or less chlorines and the congeners with retention times longer than 30 minutes usually contain 5 or more. The higher chlorine content congeners appeared to be of much lower reactivity during the photocatalytic process.

Figures 14-19 are the chromatograms from the GC/MS which was configured to search for certain ion pairs in the sediment extract. Figs 14-16 illustrate the chromatograms of congeners with 1 to 3 chlorines and Figs 17-19 illustrate the congeners with 4 or more chlorines. In addition to the dramatic decrease in the individual peak heights, the general trend relative to the experimental blank (Fig. 14) is from high to low with increasing retention times. This tendency shifts in the opposite direction for Fig. 15 and 16, which are from the samples subjected to

-27-

irradiation for 2 and 6 hours, respectively.
However, this phenomena is not observed in the higher
chlorinated congeners as illustrated in Figs 17-19.
These results provide further evidence that the lower
5 chlorinated PCB congeners are more readily decomposed
by photocatalytic process.

Table 1

Relative Changes of PCBs in Aqueous Systems Under Radiation of Sunlight in the Presence of TiO_2

Treatment	Relative Integrated Area of Chromatog.	% of Exp. Blank (original conc.)
PCB-Clay		
PCB-Clay Suspension (Blank)	1,732,642	100
Wrapped Suspension (Control I)	1,994,423	115
Wrapped Suspension with TiO_2 (Control II)	1,958,109	113
2 h exposure	399,559	23
4 h exposure	336,236	19
Sediment		
Sediment Suspension (Blank)	1,766,587	100
Suspension with TiO_2 (Control)	1,927,842	109
2 h exposure	1,286,741	73
6 h exposure	836,706	47

-29-

Example II

Escherichia coli (E. coli) was used as an index to assess the disinfection of water-borne microorganisms by sunlight irradiation in the presence of a titanium dioxide (TiO_2 , anatase) photocatalyst. With 23 minutes irradiation, more than 99% of the spiked E. coli was inactivated in water solutions. No significant changes in E. coli were observed in the irradiated control with no titanium dioxide added, or in the water solution that was not irradiated but contained titanium dioxide. The inactivation of E. coli was attributed to the generation of free hydroxyl radicals during irradiation of titanium dioxide in the aqueous solution.

Titanium dioxide used in this study was obtained from Degussa with a dominant mineralogical form of anatase. Titanium dioxide was suspended in distilled-deionized water at a concentration of 100 g/L as the stock suspension.

Escherichia coli (Wards, #85W0400) was grown on a nutrient agar slant at 37°C for 48 hours. Cells were suspended in 10.0 ml of sterile deionized water to give an optical density reading of 0.06 at 540 nm using a spectronic 20 colorimeter. Duplicate experimental and control systems were prepared by adding 9.0 ml of the cell suspension to 891 ml of sterile deionized water and distributing to each of eight sterile 250 ml Erlenmeyer screen cap flasks.

A batch study was carried out with duplicate 250 ml Erlenmeyer flasks made of Pyrex glass. A sterile teflon coated magnetic stirring bar was used in each

-30-

flask which contained 100 ml of E. coli spiked
deionized water and the system was kept homogenous
during the entire treatment period. In the titanium
dioxide treatment, 0.2 ml of titanium dioxide stock
5 suspension was pipetted into the 100 ml water and E.
coli mixture which resulted in a titanium dioxide
concentration of 0.2 g/L. Two experimental controls
were used, one with titanium dioxide but wrapped with
aluminum foil and another with no titanium dioxide
10 added, but not wrapped. An experimental blank was
set up with no addition of titanium dioxide and
wrapped with aluminum foil. Duplicates of flasks
containing the water and titanium dioxide used in the
treatments, but no E. coli, were used to check
15 background of the cells in water and titanium dioxide
suspension. All Erlenmeyer flasks used in the study
were covered with sterilized glass stoppers.

All samples including controls and blanks were
taken to the roof of a building at the State
20 University of New York at Oswego (43°N, 76.5°W) and
exposed to sunlight from 11:00 to 11:23 am on a sunny
day at a temperature of 20 +/- 1°C.

Following irradiation, samples were moved to the
laboratory and samples were immediately diluted.
25 Standard plate counts were performed on each
treatment using 10⁻⁴ M sodium phosphate, pH=6.8, as
the diluting medium and nutrient agar as the growth
medium. The samples irradiated with titanium dioxide
were diluted to 10, 100, 1000, and 10000 times before
30 one ml of diluted solution was transferred to the
petri plates. The experimental controls and blanks
were diluted to 100, 1000, and 10000 times original
concentrations. The titanium dioxide suspension
without spiked E. coli was cultured with the original

-31-

and 10 times diluted solutions. Triplicate plates were incubated at 37°C for 48 hours.

As presented in Table 2, with 23 minutes irradiation, the total averaged active cell density in the 10 and 100 times diluted solutions are 23-27 and 2-3 cell/ml, respectively. These numbers are less than 1% of the total cell density obtained from the averaged numbers from the experimental controls and blanks. Without titanium dioxide, sunlight did not affect the cell density in the aqueous solution in this short period of irradiation. E. coli cells were not disinfected in titanium dioxide suspension unless exposed to sunlight. The densities of active cells in the two experimental controls were about the same. The active cell density in the experimental blanks was lower than that of the experimental blanks, but no statistically significant difference is observed from a F test (Probability = 0.99). Therefore, it can be concluded that E. coli inactivation in water solutions is attributed to irradiation of titanium dioxide. Sunlight irradiation absent titanium dioxide did not affect E. coli and the presence of titanium dioxide in the aqueous solution did not decrease the E. coli cell density without irradiation.

Results from this experiment demonstrate the potential to disinfect microorganisms in water utilizing sunlight and titanium dioxide as a photocatalyst.

-32-

Table 2

Disinfection of Bacteria in Aqueous Solutions Irradiated with
Sunlight in the Presence of TiO_2 as a Photocatalyst

Sample Description	Cell Density ¹ cell/ml				
	Dilutions				
	x1	x10	x100	x1,000	x10,000
Blank: no TiO_2 added; no (I)			TNTC ²	164 (± 7)	18 (± 4)
irradiation (II)			TNTC	162 (± 12)	21 (± 1)
Control 1: TiO_2 (0.1 g/l); no (I)			TNTC	169 (± 6)	11 (± 2)
irradiation (II)			TNTC	179 (± 9)	20 (± 2)
Control 2: no TiO_2 added; irradiation (I)			TNTC	157 (± 10)	13 (± 3)
23 min. (II)			TNTC	146 (± 9)	13 (± 1)
TiO_2 added (0.1 g/l); irradiation (I)		23 (± 2)	3 (± 1)	0	---
23 min. (II)		27 (± 4)	2 (± 1)	0	---
TiO_2 suspension (0.1 g/l); no (I)	0	0	---	---	---
<u>E.coli</u> spiked (II)	0	0	---	---	---

¹Averaged of triplicate²TNTC - too numerous to be counted

-33-

Although preferred embodiments have been depicted and described in detail herein, it will be apparent to those skilled in the relevant art that various modifications, additions, substitutions and
5 the like can be made without departing from the spirit of the invention and these are therefore considered to be within the scope of the invention as defined by the following claims.

-34-

List of References

1. J.H. Carey et al., Bull Environ Contami
Toxicol 16:697-701 (1976).
2. G. Occhiucci and A. Patacchiola, Chemosphere
5 11:255-262 (1982).
3. S. Tunesi and M.A. Anderson, Chemosphere
16:1447-1456 (1987).
4. E. Pelizzetti et al., Chemosphere 17:499-510
(1988).
- 10 5. G.A. Epling et al., Chemosphere 17:1355-1362
(1988).
6. G.A. Epling et al., Chemosphere 22:959-962
(1991).
7. T. Sheili et al., Chemosphere 22:1053-1062
15 (1991).
8. G.A. Epling et al., Environ Sci Technol
22:952-956 (1988).
9. J. Hawari et al., Chemosphere 22:189-199
(1991).
- 20 10. J.C. Ireland et al., Applied and
Environmental Microbiology 59:1668-1670 (1993).
11. P.E. Menassa, Environmental Technology
Letters 9 (1988).
12. B.G. Oliver and J.H. Carey,
25 "Photodegradation of wastes and pollutants in aquatic
environment" in Homogeneous and Heterogeneous
Photocatalysis, E. Pelizzetti and N. Serpone (eds.),
Reidel Publishing Co. (1986).
13. D.F. Ollis et al., Environ Sci & Technol
30 25:1523-1529 (1991).
14. E. Pelizzetti et al., The Science of the
Total Environ. 123:161-169 (1992).
15. D.L. Sediak and A.W. Andren, Environ Sci &
Technol 25:1419-1427 (1991).

-35-

16. K. Tanaka et al., J Photochem and Photobiol
48:155-159 (1989a).
17. K. Tanaka et al., New Journal of Chemistry
13:5-7 (1989b).
- 5 18. A.R. Mudambi and J.P. Hassett, Chemosphere
17:1133-1146 (1988).
19. G. Durand et al., Toxicol Environ Chem
32:55-62 (1991).
20. O.C. Zafiriou et al., Environ Sci & Tech
10 18:358A-371A (1984).
21. J. Kochany, Chemosphere 24:1119-1126
(1992).
22. K.B. Woodburn et al., Environ Toxicol Chem
12:43-55 (1993).

-36-

What is claimed is:

1 1. An apparatus for photocatalytic degradation
2 of contaminants in solid material comprising:
3 means for containing a solid material;
4 means for agitating said solid material within
5 an aqueous source of free radicals, thereby
6 separating said solid material into a first portion
7 suspended in said aqueous source and a second portion
8 deposited below said aqueous source; and
9 means for simultaneously exposing said first
10 portion to a photoactivatable catalyst and light
11 energy.

1 2. The apparatus of claim 1 wherein said solid
2 material comprises sediment deposited below water.

1 3. The apparatus of claim 2 wherein said water
2 comprises a lake or pond. N

1 4. The apparatus of claim 1 wherein said means
2 for containing comprises a caisson. Y

1 5. The apparatus of claim 4 wherein said means
2 for agitating comprises a dredge located within said
3 solid material. N

1 6. The apparatus of claim 4 wherein said means
2 for simultaneously exposing comprises a light
3 penetrable portion of said caisson and a source of
4 light energy positioned outside said caisson at said
5 light penetrable portion. Y

-37-

1 7. The apparatus of claim 4 wherein said means
2 for simultaneously exposing comprises a source of
3 light energy positioned within said caisson. ✓

1 8. The apparatus of claim 4 further comprising
2 means to contain any volatiles released from said
3 caisson. ~

1 9. The apparatus of claim 1 wherein said means
2 for containing comprises a reactor housing. 7

1 10. The apparatus of claim 9 wherein said solid
2 material comprises solid material deposited below
3 water and further comprising means for removing said
4 solid material to said reactor housing. ~

1 11. The apparatus of claim 10 wherein said
2 means for removing comprises a dredge connected from
3 said solid material to said reactor housing. ✓

1 12. The apparatus of claim 9 wherein said means
2 for agitating comprises movable baffles mounted
3 within said reactor housing. ✓

1 13. The apparatus of claim 12 wherein said
2 movable baffles are mounted on a rotatable boom
3 mounted within said reactor housing. ~

1 14. The apparatus of claim 9 wherein said means
2 for simultaneously exposing comprises a light
3 penetrable portion of said reactor housing and a
4 source of light energy positioned outside said
5 reactor housing at said light penetrable portion. ~

-38-

1 15. The apparatus of claim 9 wherein said means
2 for simultaneously exposing comprises a source of
3 light energy positioned within said reactor housing.

1 16. The apparatus of claim 9 further comprising
2 means to contain any volatiles released from said
3 reactor housing.

1 17. The apparatus of claim 16 wherein said
2 means to contain any volatiles comprises a granular
3 activated carbon trap.

1 18. The apparatus of claim 9 further comprising
2 means to remove said first portion to a second
3 reactor housing.

1 19. The apparatus of claim 18 wherein said
2 second reactor housing comprises:
3 means for containing said first portion;
4 means for agitating said first portion within an
5 aqueous source of free radicals; and
6 means for simultaneously exposing said first
7 portion to a photoactivatable catalyst and light
8 energy.

1 20. The apparatus of claim 18 wherein said
2 means to remove said first portion comprises a pipe
3 connected from said reactor housing to said second
4 reactor housing.

1 21. The apparatus of claim 20 further
2 comprising a pump to force said first portion through
3 said pipe.

-39-

1 22. The apparatus of claim 9 further comprising
2 means to remove said second portion to a second
3 reactor housing.

1 23. The apparatus of claim 22 wherein said
2 second reactor housing comprises:
3 means for containing said second portion;
4 means for agitating said second portion within
5 an aqueous source of free radicals; and
6 means for simultaneously exposing said second
7 portion to a photoactivatable catalyst and light
8 energy.

1 24. The apparatus of claim 22 wherein said
2 means to remove said second portion comprises an
3 auger connected from said reactor housing to said
4 second reactor housing.

1 25. The apparatus of claim 9 further comprising
2 means to contain spills from said reactor housing.

1 26. The apparatus of claim 25 wherein said
2 means to contain spills comprises a containment
3 housing surrounding said reactor housing.

1 27. The apparatus of claim 1 further comprising
2 a source of light energy.

1 28. The apparatus of claim 27 wherein said
2 source of light energy comprises sunlight. ~

1 29. The apparatus of claim 27 wherein said
2 source of light energy comprises an artificial light
3 source. ~

-40-

1 30. The apparatus of claim 29 wherein said
2 artificial light source comprises a sun lamp.

1 31. The apparatus of claim 1 further comprising
2 means for introducing a photoactivatable catalyst
3 into said means for containing a solid material.

1 32. The apparatus of claim 9 further comprising
2 means to grind said solid material prior to
3 containing said solid material in said reactor
4 housing.

1 33. The apparatus of claim 1 further comprising
2 means for simultaneously exposing said second portion
3 to a photoactivatable catalyst and light energy.

1 34. An apparatus for photocatalytic degradation
2 of contaminants in solid material comprising:
3 means for containing a solid material;
4 means for agitating said solid material within
5 an aqueous source of free radicals; and
6 means for simultaneously exposing said solid
7 material to a photoactivatable catalyst and light
8 energy.

1 35. The apparatus of claim 34 wherein said
2 means for containing comprises a reactor housing.

1 36. The apparatus of claim 35 wherein said
2 means for agitating comprises movable baffles mounted
3 within said reactor housing.

-41-

1 37. The apparatus of claim 36 wherein said
2 movable baffles are mounted on a rotatable boom
3 mounted within said reactor housing.

1 38. The apparatus of claim 36 wherein said
2 movable baffles are plow-shaped.

1 39. The apparatus of claim 35 wherein said
2 means for simultaneously exposing comprises a light
3 penetrable portion of said reactor housing and a
4 source of light energy positioned outside said
5 reactor housing at said light penetrable portion.

1 40. The apparatus of claim 35 wherein said
2 means for simultaneously exposing comprises a source
3 of light energy positioned within said reactor
4 housing.

1 41. A method for photocatalytic degradation of
2 contaminants in solid material, said method
3 comprising:
4 selecting a solid material containing
5 contaminants therein;
6 placing said solid material in a reactor housing
7 containing an aqueous source of free radicals;
8 agitating said solid material in said aqueous
9 source of free radicals, so as to separate said solid
10 material into a first portion suspended in said
11 aqueous source and a second portion deposited below
12 said aqueous source;
13 introducing a photoactivatable catalyst into
14 said reactor housing; and
15 exposing said photoactivatable catalyst to light
16 energy, thereby causing reaction of said catalyst

-42-

17 with said aqueous source of free radicals to generate
18 said free radicals, wherein said free radicals
19 contact said first portion of said solid material
20 suspended in said aqueous source and degrade the
21 contaminants contained therein.

1 42. The method of claim 41 wherein said solid
2 material is selected from the group consisting of
3 sediment, soil, and sludge.

1 43. The method of claim 41 wherein said
2 contaminant comprises an organic contaminant.

1 44. The method of claim 43 wherein said organic
2 contaminant comprises polychlorinated biphenyls.

1 45. The method of claim 43 wherein said organic
2 contaminant comprises a microorganism.

1 46. The method of claim 45 wherein said
2 microorganism comprises Escherichia coli.

1 47. The method of claim 41 wherein said
2 contaminant comprises an inorganic contaminant.

1 48. The method of claim 47 wherein said
2 inorganic contaminant comprises a metal.

1 49. The method of claim 41 wherein said
2 contaminant is selected from the group consisting of
3 pesticides, insecticides, and fungicides.

1 50. The method of claim 41 wherein said aqueous
2 source of free radicals comprises water.

-43-

1 51. The method of claim 41 wherein said
2 photoactivatable catalyst comprises a semiconductive
3 material.

1 52. The method of claim 51 wherein said
2 semiconductive material comprises titanium dioxide.

1 53. The method of claim 51 wherein said
2 semiconductive material comprises zinc oxide.

1 54. The method of claim 41 wherein said light
2 energy comprises sunlight.

1 55. The method of claim 41 wherein said light
2 energy comprises ultraviolet light.

1 56. The method of claim 41 wherein said light
2 energy comprises artificial light.

1 57. The method of claim 41 further comprising:
2 removing said second portion of said solid
3 material to a second reactor housing; and
4 simultaneously contacting said second portion of
5 said solid material with an aqueous source of free
6 radicals, a photoactivatable catalyst, and light
7 energy, wherein resulting reaction of said catalyst
8 with said aqueous source of free radical generates
9 said free radicals, and wherein said free radicals
10 contact said second portion of said solid material
11 and degrade the contaminants contained therein.

1 58. The method of claim 57 wherein said
2 removing of said second portion comprises utilizing

-44-

3 an auger which travels from said deposited second
4 portion to said second reactor housing.

1 59. The method of claim 41 further comprising
2 transferring a fraction of said first portion to a
3 second reactor housing, wherein said fraction is
4 simultaneously contacted with an aqueous source of
5 free radicals, a photoactivatable catalyst, and light
6 energy, wherein resulting reaction of said catalyst
7 with said aqueous source of free radical generates
8 said free radicals, and wherein said free radicals
9 contact said fraction of said first portion of said
10 solid material and degrade the contaminants contained
11 therein.

1 60. The method of claim 59 wherein said
2 transferring of a fraction of said first portion
3 utilizes a pipe and wherein said transferring occurs
4 by gravity.

1 61. The method of claim 59 wherein said
2 transferring of a fraction of said first portion
3 utilizes a pipe and a pump and wherein said
4 transferring occurs by force of said pump.

1 62. The method of claim 41 wherein said
2 exposing of said photoactivatable catalyst to light
3 energy occurs at the surface of said aqueous source
4 of free radicals within said reactor housing.

1 63. The method of claim 59 further comprising
2 agitating said second portion of said solid material
3 so as to separate said second portion into a further
4 suspended portion and a further deposited portion,

-45-

5 said further suspended portion being degraded by said
6 free radicals.

1 64. The method of claim 41 further comprising
2 removing degraded contaminants from said reactor
3 housing.

1 65. The method of claim 64 wherein said
2 removing degraded contaminants utilizes a granular
3 activated carbon filter.

1 66. The method of claim 41 further comprising
2 removing degraded solid material from said reactor
3 housing.

1 67. The method of claim 66 wherein said
2 removing degraded solid material utilizes a discharge
3 channel.

1 68. The method of claim 41 further comprising
2 exposing said photoactivatable catalyst in the
3 presence of light to a photocatalysis enhancer.

1 69. The method of claim 68 wherein said
2 photocatalysis enhancer comprises hydrogen peroxide.

1 70. The method of claim 41 further comprising
2 treating said solid material with a surfactant prior
3 to agitation so as to concentrate said contaminants
4 on said surfactant.

1 71. The method of claim 41 further comprising
2 treating said photoactivatable catalyst so that said
3 catalyst can be recovered.

-46-

1 72. The method of claim 71 wherein said
2 treating comprises attaching said catalyst to a
3 magnetic material.

1 73. A method for photocatalytic degradation of
2 contaminants in solid material, said method
3 comprising:
4 selecting a solid material containing
5 contaminants therein;
6 placing said solid material in a reactor housing
7 containing an aqueous source of free radicals;
8 agitating said solid material in said aqueous
9 source of free radicals;
10 introducing a photoactivatable catalyst into
11 said reactor housing; and
12 exposing said photoactivatable catalyst to light
13 energy, thereby causing reaction of said catalyst
14 with said aqueous source of free radicals to generate
15 said free radicals, wherein said free radicals
16 contact said solid material and degrade the
17 contaminants contained therein.

FIG. 1

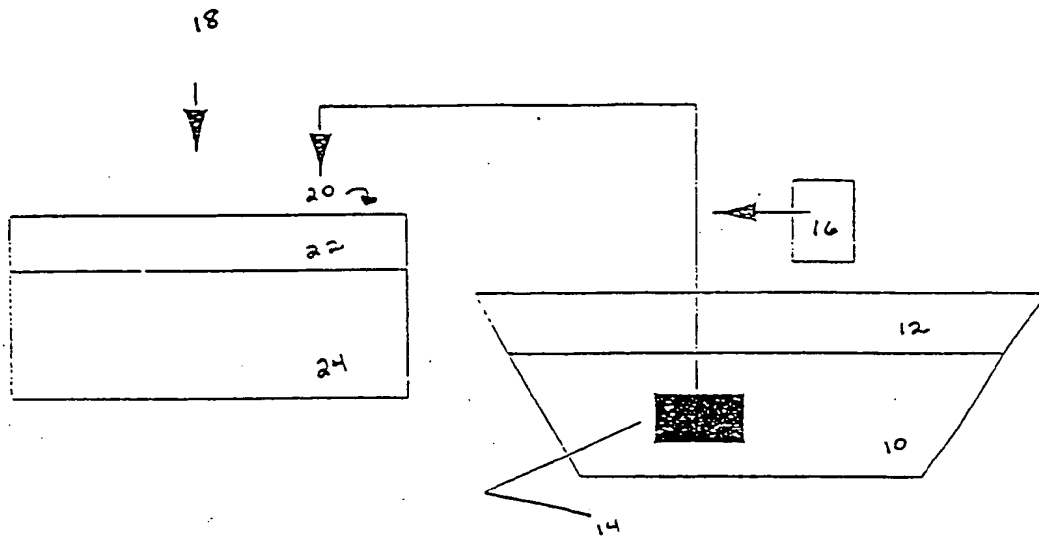
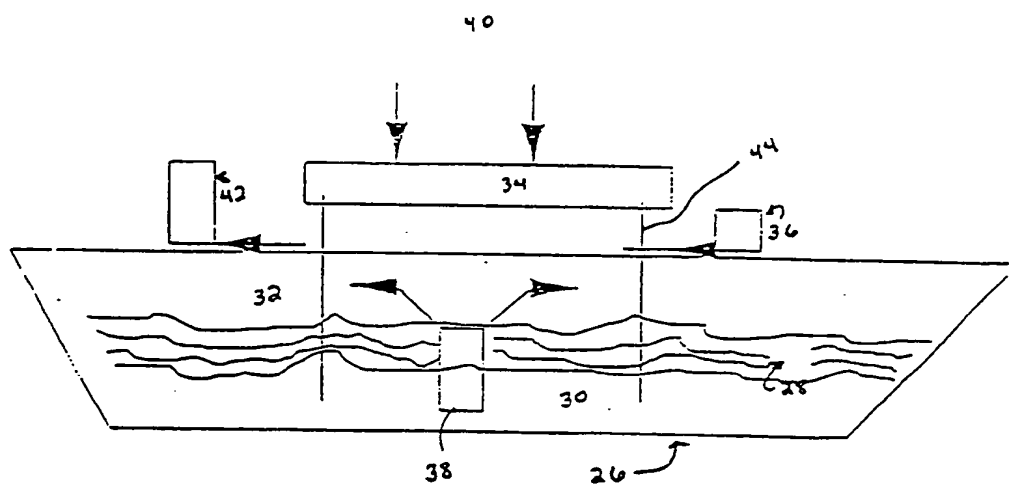


FIG. 2



2/15

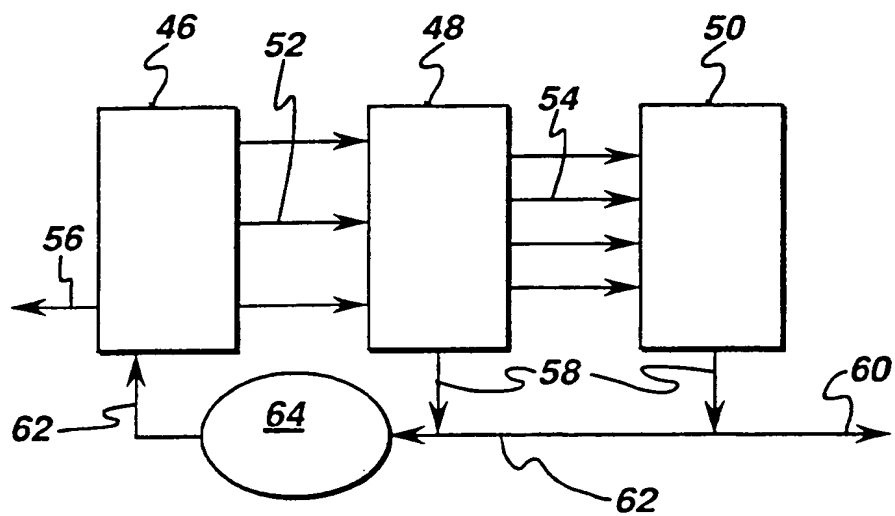


fig. 3

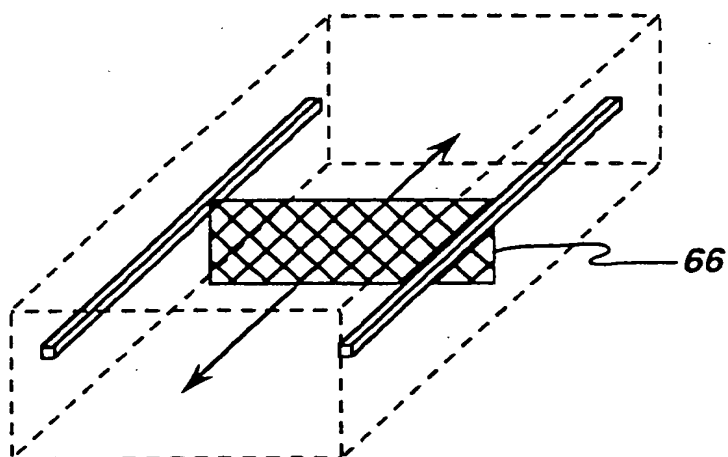
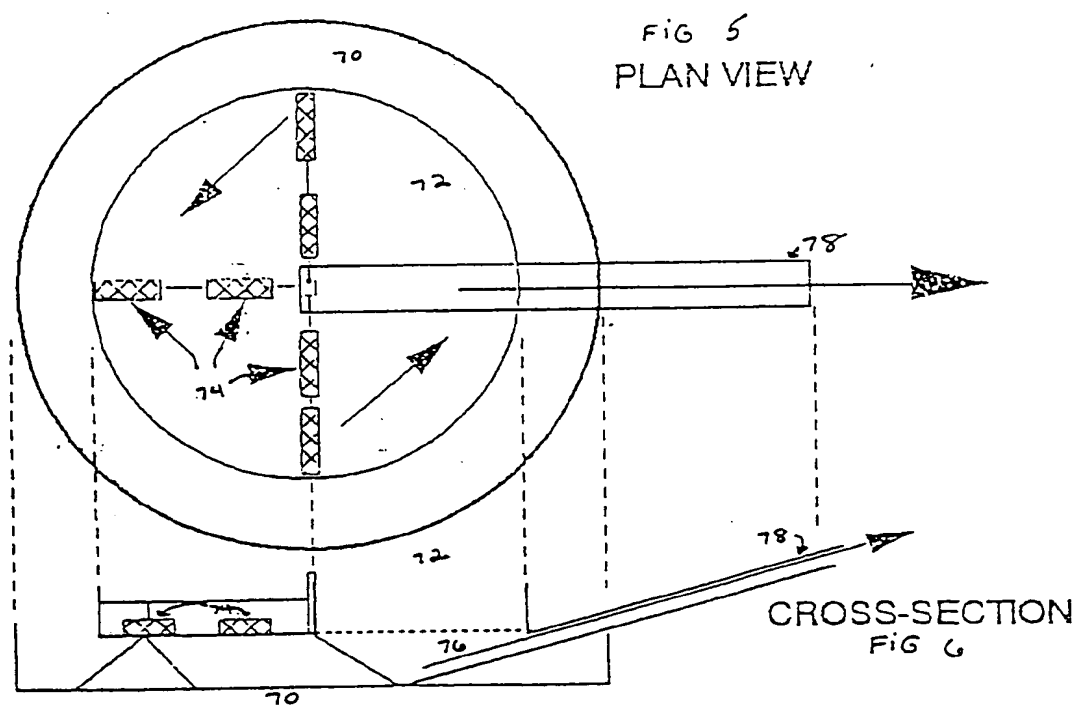


fig. 4

RECTIFIED SHEET

1/15



4/15

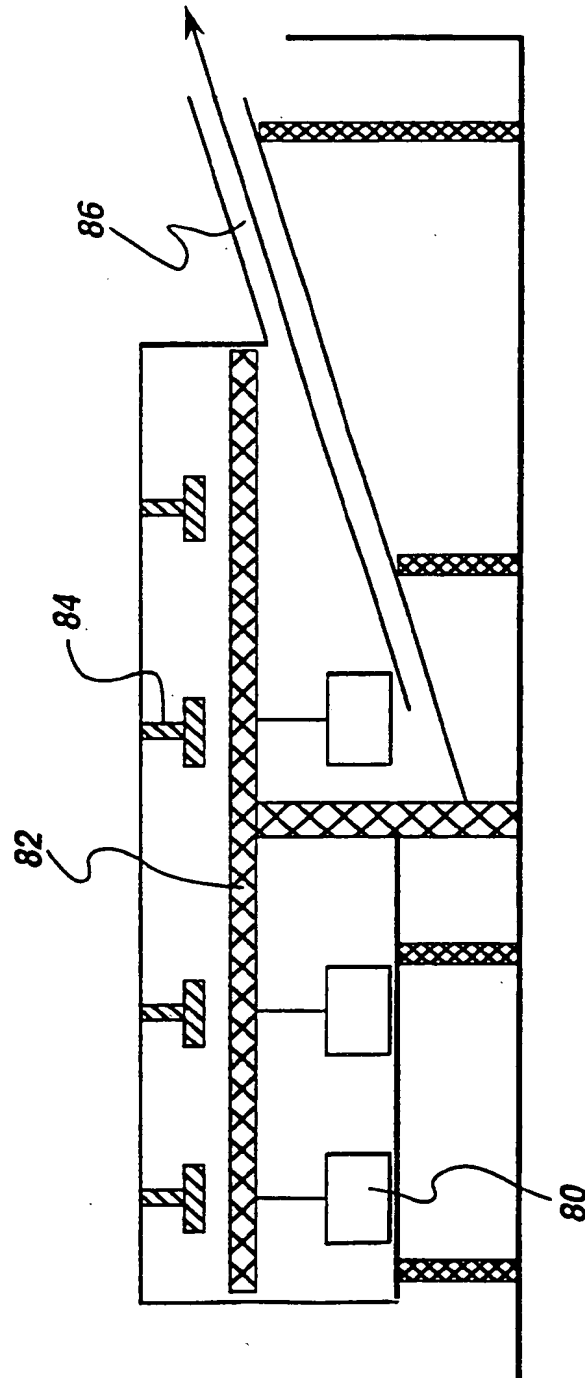


fig. 7

RECTIFIED SHEET

FIG. 8

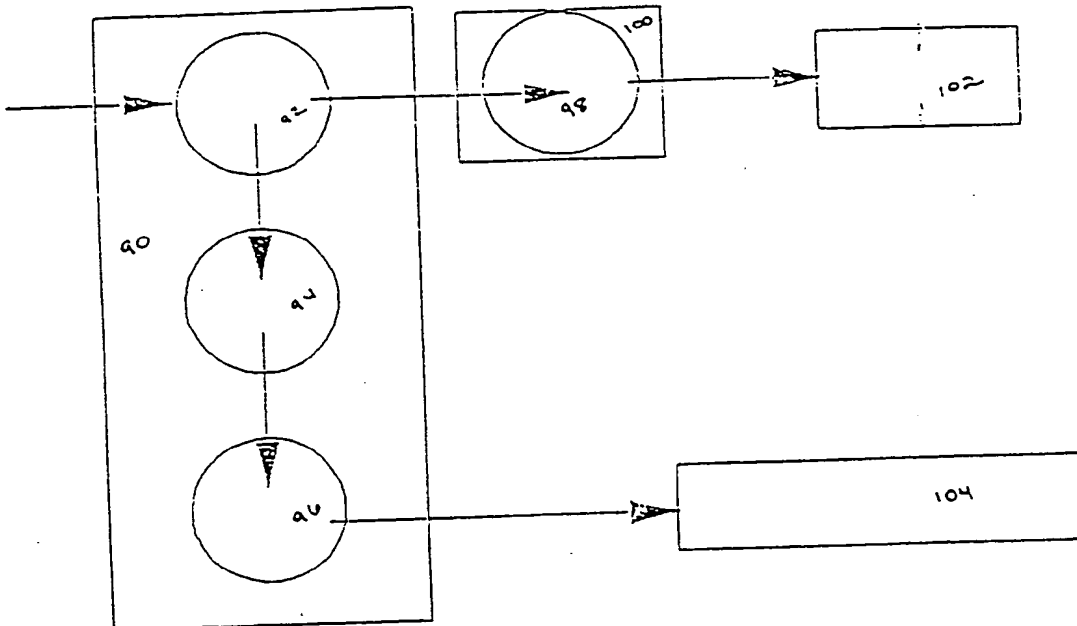
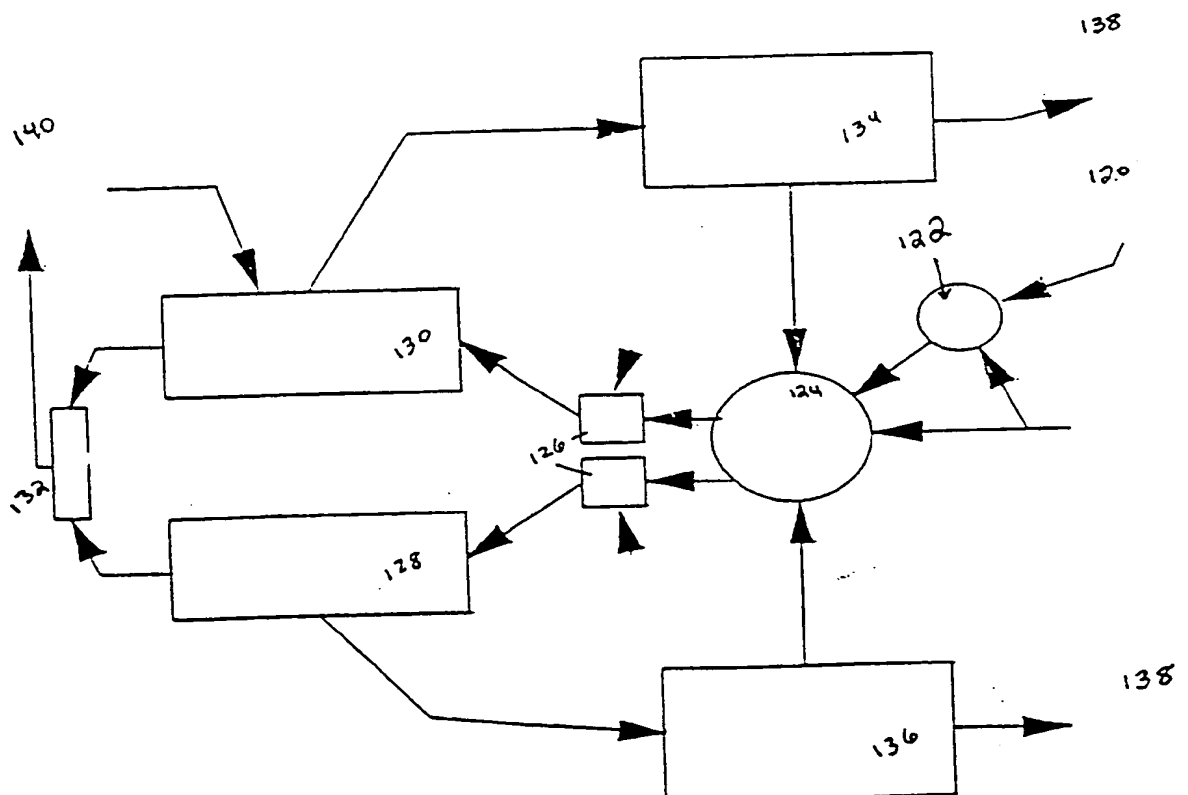


FIG. 9



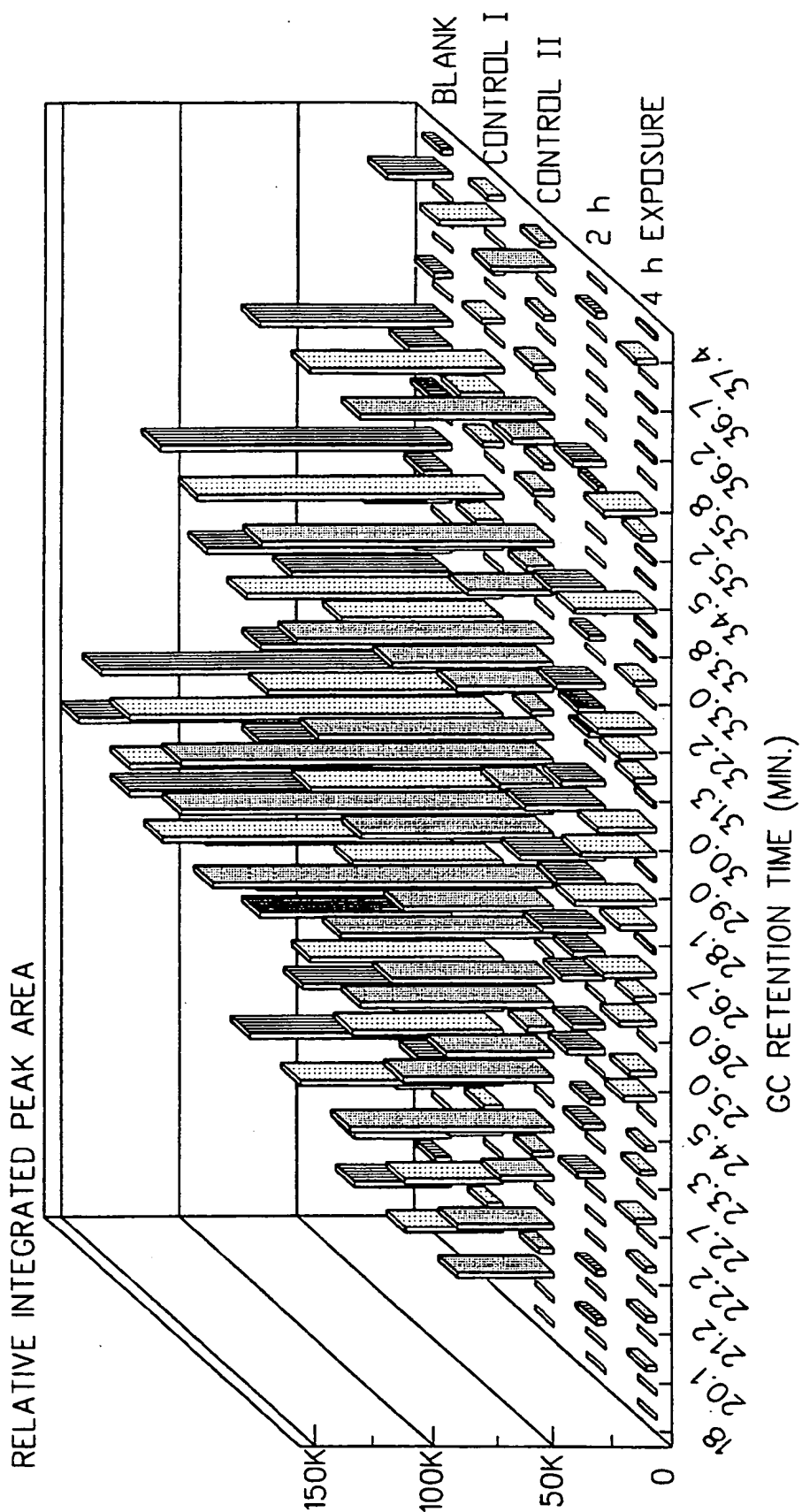


fig. 10

RECTIFIED SHEET

7/15

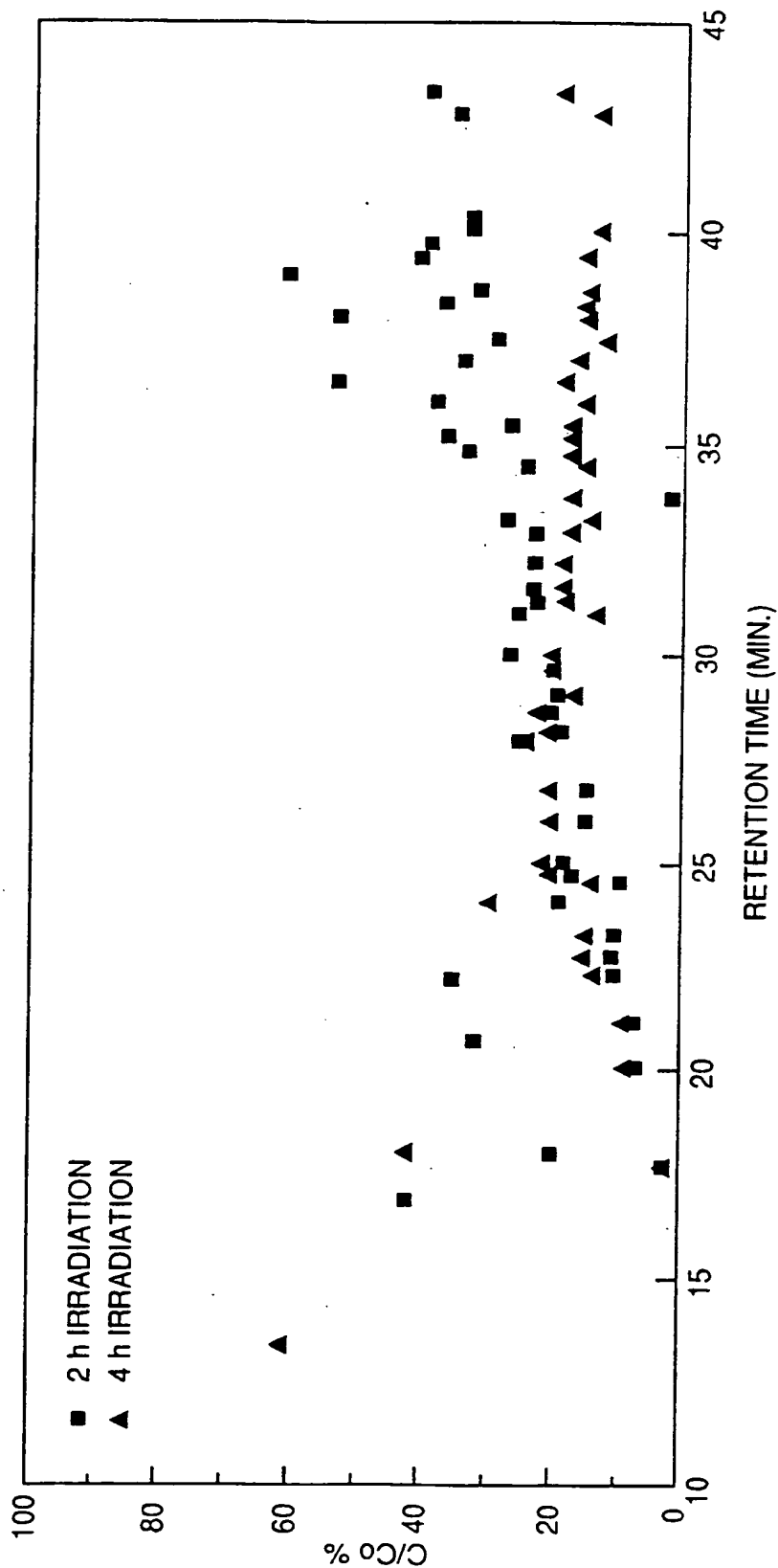


fig. 11

RECTIFIED SHEET

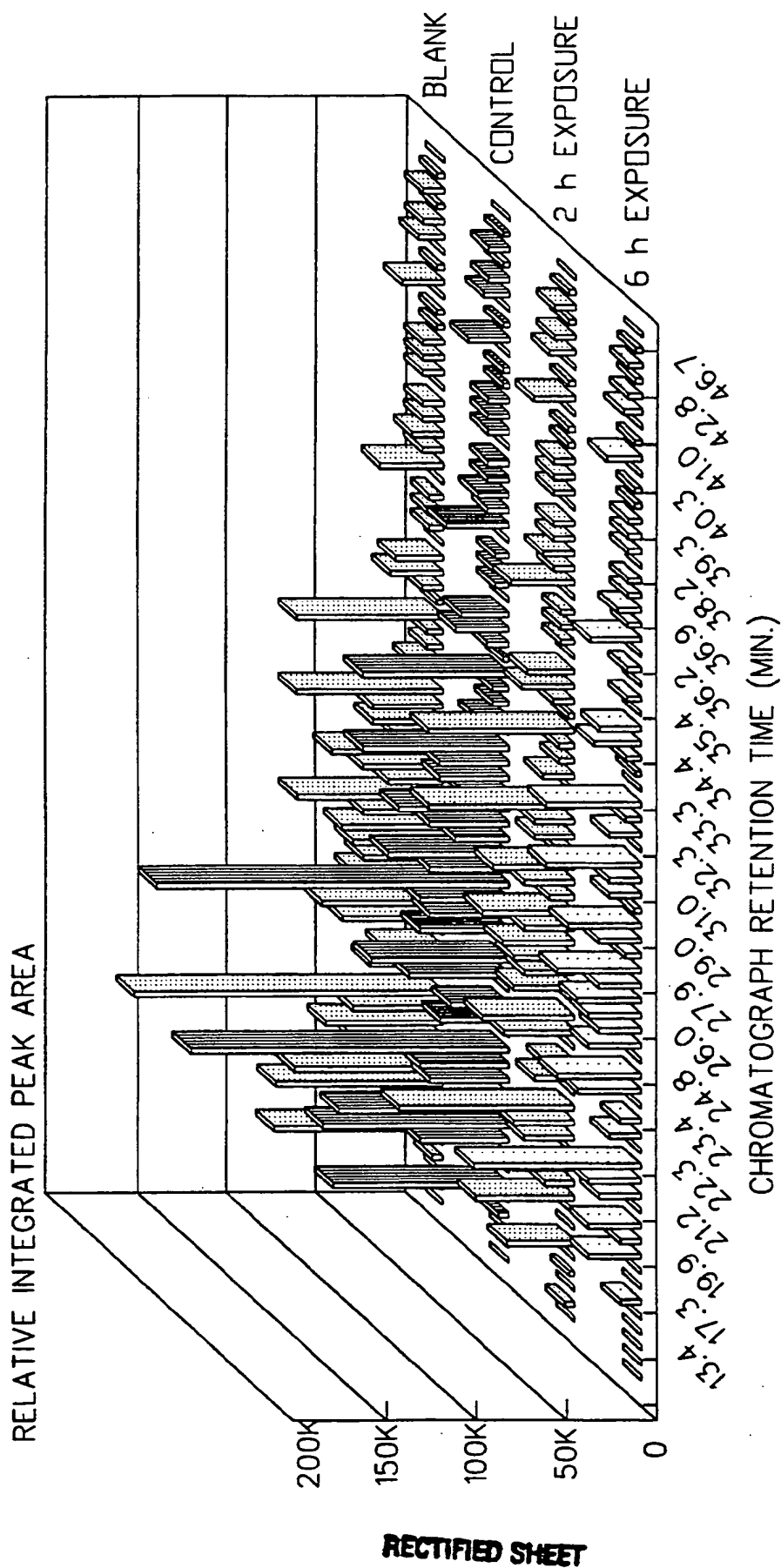


fig. 12

9/15

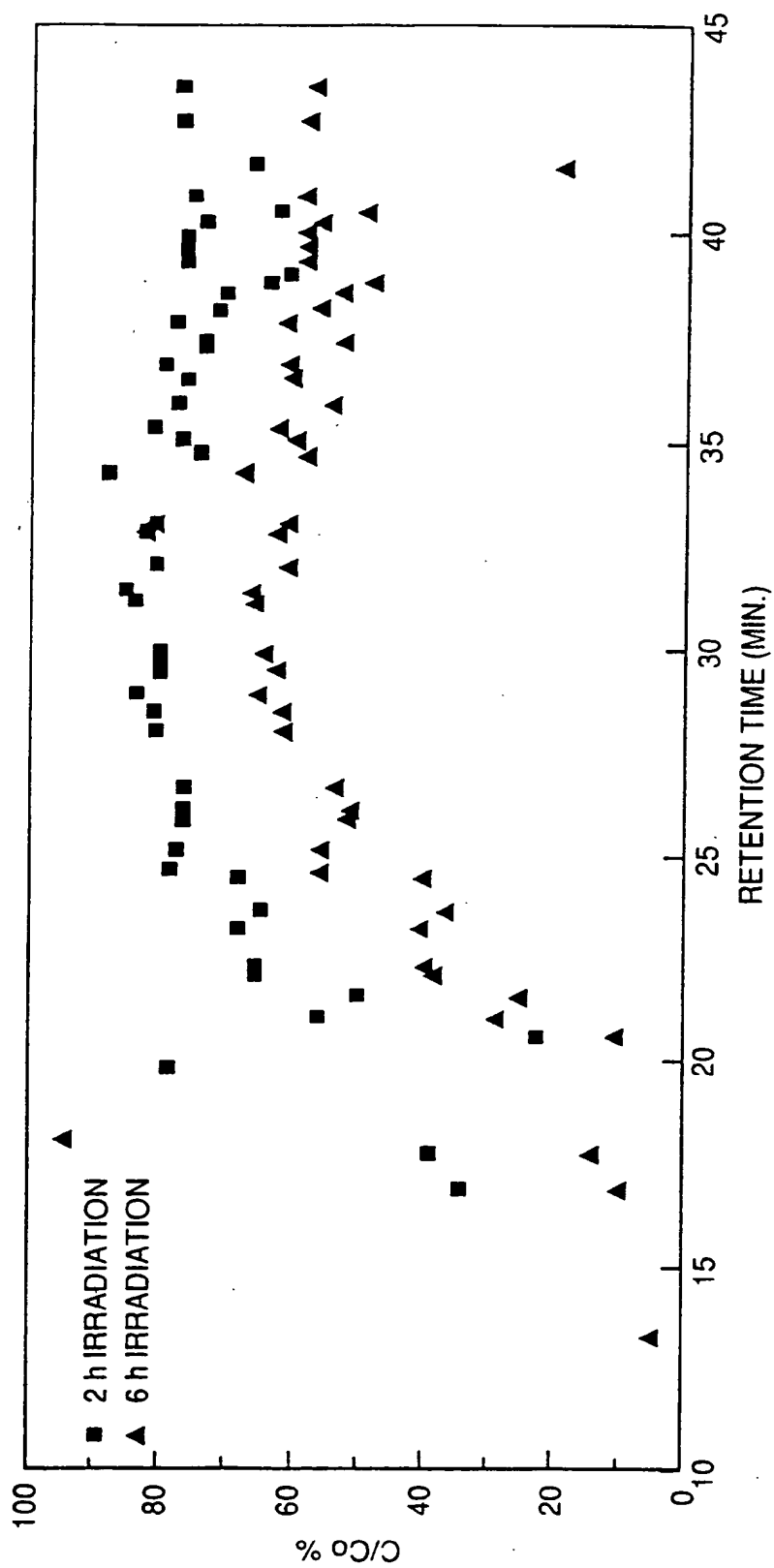


fig. 13

RECTIFIED SHEET

10/15

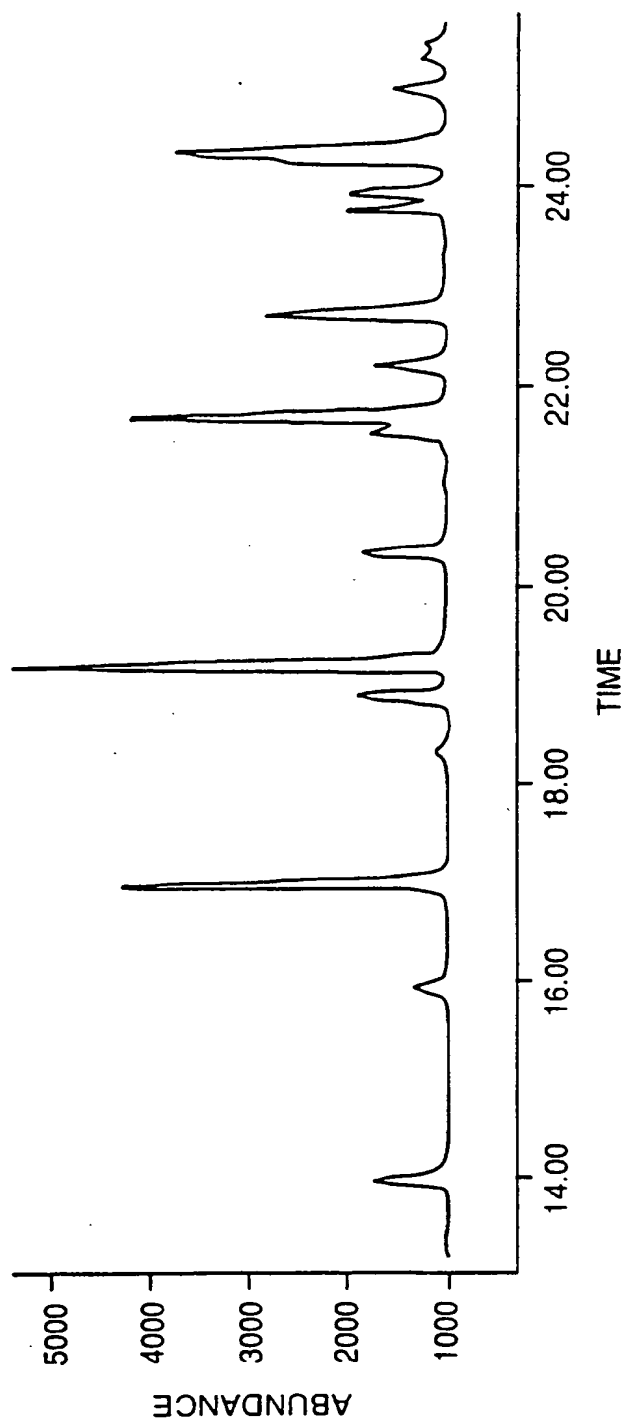


fig. 14

RECTIFIED SHEET

11/15

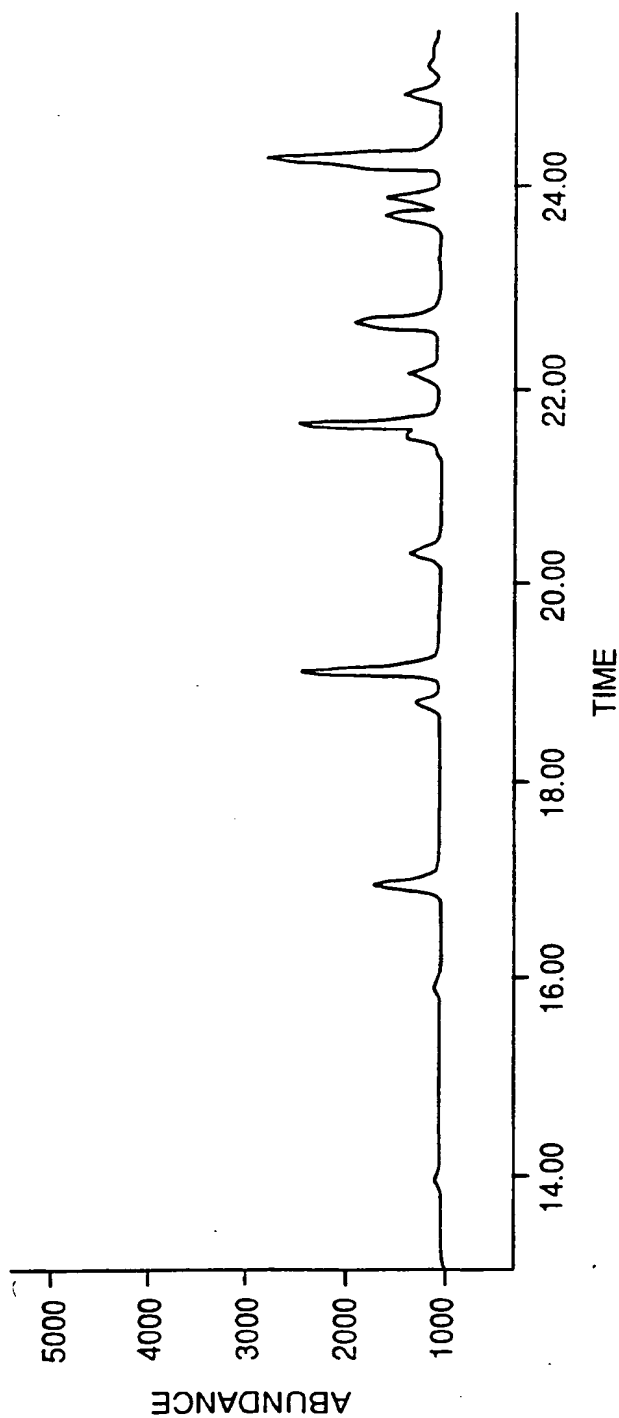


fig. 15

RECTIFIED SHEET

12/15

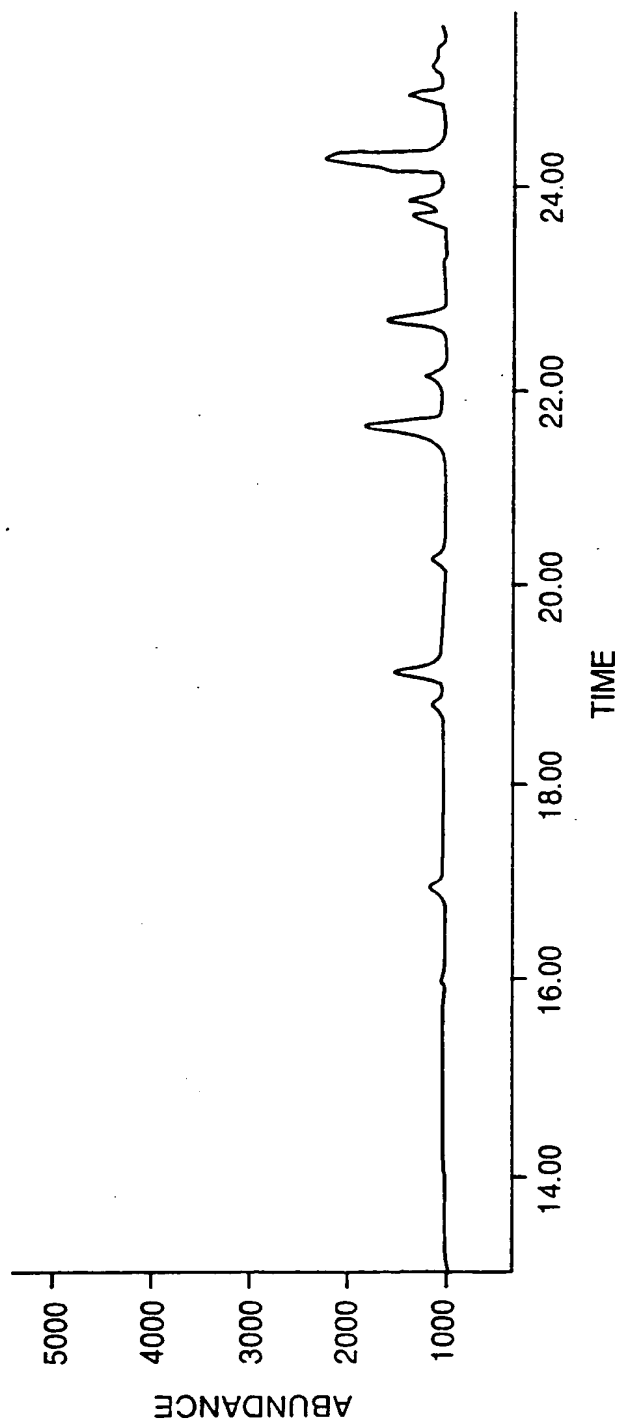


fig. 16

RECTIFIED SHEET

13/15

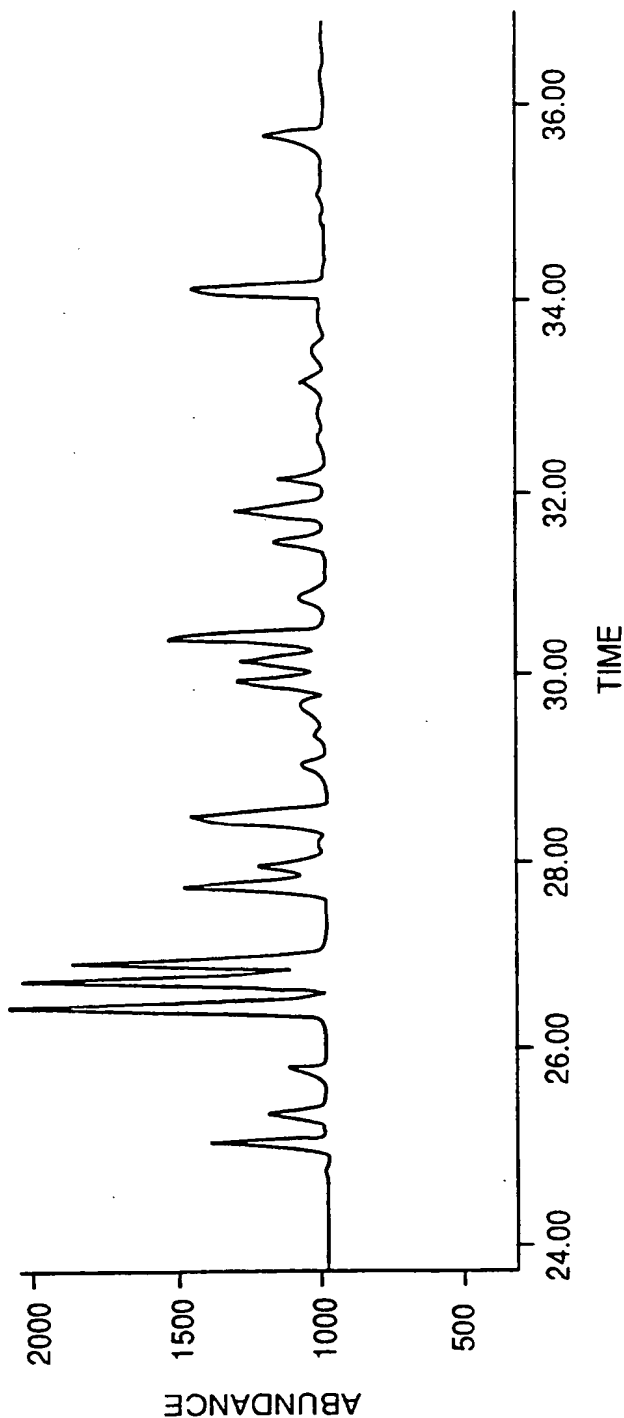


fig. 17

RECTIFIED SHEET

14/15

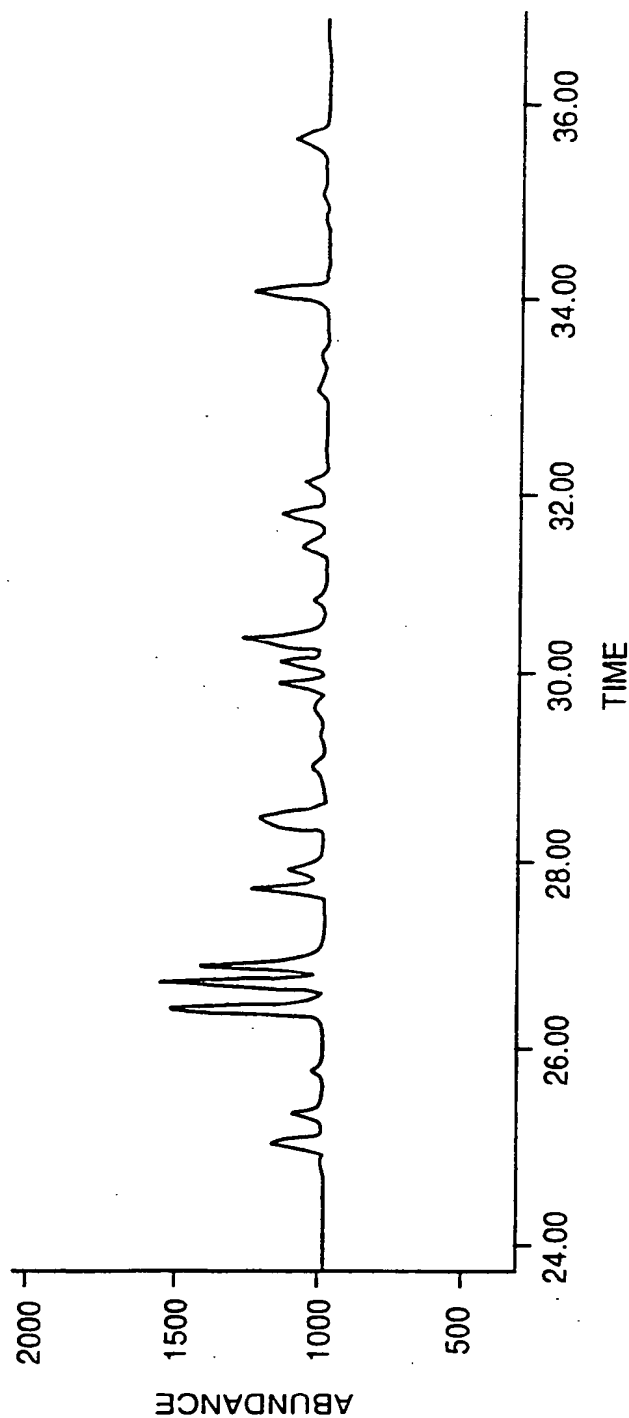


fig. 18

RECTIFIED SHEET

15/15

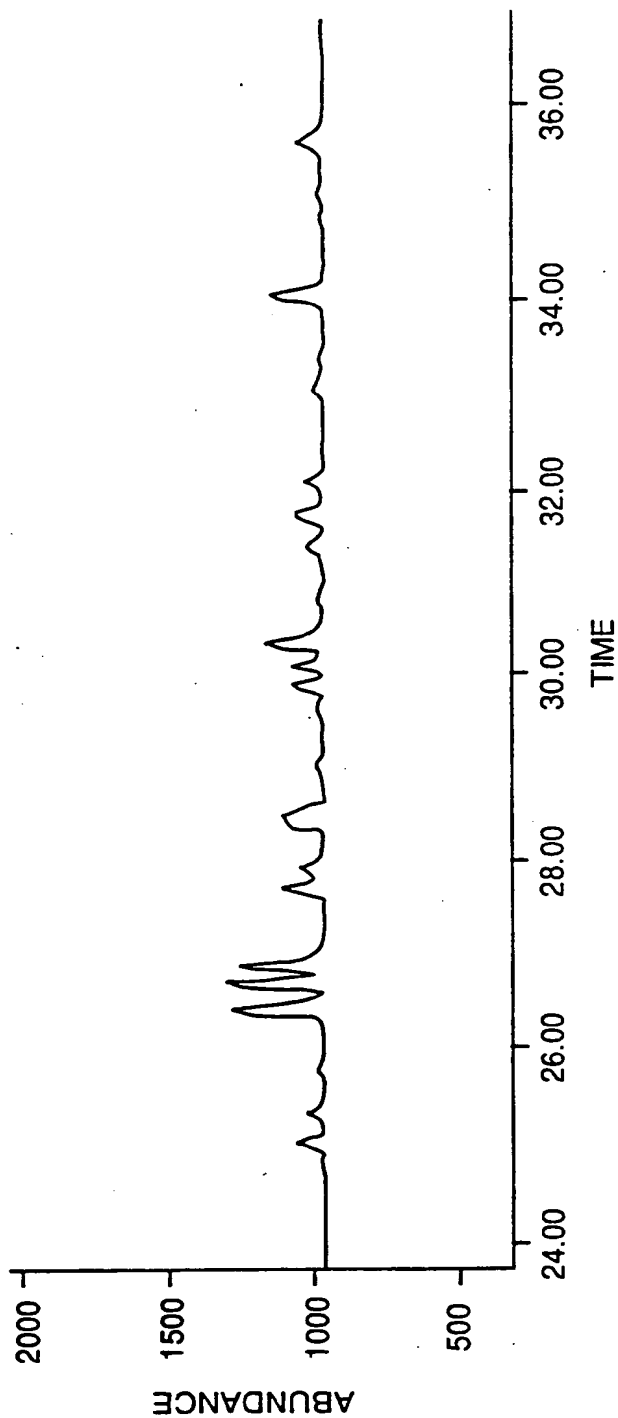


fig. 19

RECTIFIED SHEET

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/12357

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B01J 19/08; C07B 63/00

US CL : 422/186.3; 204/158.20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 204/157.15, 158.20, 158.21; 210/748, 759;
588/207, 210, 227; 422/186.3Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

Degradation, degrading, removal, removing, light, irradiation agitating, ultrasonic, sediment, soil, sludge, titanium dioxide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 4,861,484 (Lichtin et al.) 29 August 1989, Col. 14, lines 37-47; col. 14 lines 45-47; abstract; col. 9, lines 35-43; col. 11 Table III; Col. 12, lines 40-51; col. 14, lines 37-66; Col. 7, lines 36-39; Col. 11, lines 8-11 and lines 23-25, and lines 53-54.	1-73
Y	US,A, 4,978,508 (Hansen et al.) 18 December 1990, abstract; col. 2, lines 37-46, line 66; col. 3, lines 14-15, 20-27, 64-68; to col. 4, lines 1-3; col. 6, lines 5-51.	1-73
A	US,A, 4,793,931 (Stevens et al.) 27 December 1988.	None

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

&

document member of the same patent family

Date of the actual completion of the international search

28 NOVEMBER 1994

Date of mailing of the international search report

13 FEB 1995

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

JOHN NIEBLING

Telephone No. (703) 308-2505

Form PCT/ISA/210 (second sheet)(July 1992)*